

Transients in Plastic Instabilities during Thermo-mechanical reversals in an Additively Manufactured Ti6Al4V

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Degree

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DEDICATION

*To my wonderful parents,
Jacqueline and Kumar
my sister & family,
Rohit, Samantha and Ceeya
and to my dear husband,
Lamuel*

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ABSTRACT

A complex interaction of process variables in an evolving geometry during Additive Manufacturing (AM), can bring about spatial and temporal transients of temperature and stress, i.e., $\Sigma T(x,y,z,\sigma,time)$ within each layer in a part. Although AM shares commonalities with conventional processing techniques such as casting, welding and thermo-mechanical process, published literature has shown that the steady-state conditions are not strictly valid during AM process. Macro-scale fluctuations of thermal gradients (dT/dx : 10^3 to 10^7 K/m) combined with local changes in thermal expansion coefficients, crystallographic strains and localized stress-strain constitutive properties in conjunction with thermal cycles, can bring about a plastic strain gradients within the part. In the current scope of AM literature, microstructural gradients, defects and textural variations in an AM build have not been correlated to the dynamic flow behavior as a result of fluctuating macro and micro-scale phenomenons, i.e., temperature reversals and associated thermal stresses brought about by large thermal gradients and transformation strains. The current research focuses on understanding the thermo-mechanical-metallurgical aspect of AM during complex TM gyrations.

In this research, we analyzed the behavior of an AM Ti6Al4V alloy under externally imposed thermo-mechanical (TM) reversals between 400 °C and 650/700°C with alternating compressive and tensile strains (0.8%, 1.0%, 1.2%). The macro stress-strain response resulted in an overall softening behavior with an increase in the β phase fraction. Computational thermodynamic and diffusion models validated this increased β phase stability due to the added stored energy in the α phase, triggering a phase transformation. A quantitative analysis of the interface concentration profile indicated that the $\alpha \rightarrow \beta$ phase transformation occurred via a reconstructive mode. The ex-situ analyses are then corroborated with a time-resolved study using High Energy X-ray diffraction where the preferential plastic strain accumulation between the α and β phases is rationalized. The new insights on the coupling between micro-scale phase stability of the α and β phases and associated elemental distributions with macro-scale softening in a sample subject to TM gyrations, is indeed relevant to the physical metallurgy of alloys processed via AM. The phenomenon's outlined

in this research is pertinent to the description of history-dependent material flow properties in two (or more) phase alloy system during complex thermal and mechanical signatures, such as experienced during AM.

Keywords: *Additive Manufacturing, E-PBF system, α/β Ti6Al4V alloy, Cyclic Thermo-mechanical reversals, Plastic strain accumulation, Neutron Diffraction Analysis, Atom Probe tomography, High Energy X-ray diffraction, Computational Thermodynamic models - ThermoCalc[®] and DICTRA[®]*

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CHAPTER 1

Introduction

Over the last several years, research in the field of metal Additive Manufacturing (AM) has grown dramatically, with significant advancements made possible by in-situ measurements combined with ex-situ characterization of manufactured components. The unique capability of AM is its ability to design, create and produce complex and intricate components in a one-step process. Additional benefits of material efficiency, a wide variety of materials selection and short lead times has advanced AM into the industrial sector with real-life applications [5]. The Aerospace sector is one of the earliest adopters of AM technologies with applications such as rapid tooling and repair and the fabrication of complex geometries and consolidated parts. A classical application is of Titanium alloy in the aerospace field, mainly in air-frames and aero-engines. One of the principal reasons to additively manufacture Titanium is to reduce their buy-to-fly ratio [6]. The buy-to-fly ratio is the weight ratio between the raw material used for a part to the actual weight of the component. With current conventional methods of production, the buy-to-fly ratio currently stands at about 15 – 20. The AM processing route proves to be an ideal manufacturing method to drastically reduce this ratio, which is a huge benefit to the aerospace industry in terms of cost reduction. Metal AM also poses great opportunities for the automotive industry where the fabrication of unique parts of old classic cars can be done, in addition to the fabrication of light weight and complex parts

with improved production lead times [7]. For instance, BMW launched their i8 Roadster that featured a lightweight metal AM cover carrier, made from an Aluminum alloy using the powder bed fusion AM system [8]. Likewise, many other OEM's such as Honda, GM and Ford have all incorporated AM fabricated parts and developed research facilities to further AM parts in automotives [9].

The fundamental science behind metal Additive Manufacturing draws many similarities to multi-pass welding, where the weld metal and surrounding heat-affected-zones are subjected to repeated thermal cycling from successive deposition of filler metals. What differentiate AM from other welding techniques is the complex thermal+mechanical+chemical conditions that arise in each voxel across the volume of a cube during fabrication. Additional control of process parameters such as the control over beam velocity and beam power, scan strategies such as, a bi-directional linear scan versus a randomized spot melt scan, complex geometrical features and vast selection of alloy compositions, adds to the complexity of spatial and temporal thermal signatures in an AM build. To provide more context to the above statement, a typical Electron Beam Powder Bed Fusion (E-PBF) process is reviewed [10]. The E-PBF process starts with the pre-heating of a powder layer, followed by the melting of the powders as per a path file of a geometry specified by a CAD model. A layer of powder is then raked over it and this process continues till the part is built bottom-up. With the additional build-up of layers, adjacent melt areas and previous layers experience multiple thermal cycles between the liquidus temperature ($T_{melting}$) of the alloy) and the pre-heat temperature maintained [11]. Metal alloy are highly versatile in nature and many metal alloy systems comprise of 2 or more phases and/or constituents that stabilize at different temperatures on cooling from the $T_{melting}$ temperature at specified cooling rates. For instance, in the Ti6Al4V system, a BCC β phase forms on cooling below the $T_{melting}$ at 1660 °C. On further cooling, the BCC β transforms to a HCP α phase at the $\beta_{transus}$

temperature of 990 °C. Depending on the rate of cooling, different morphologies of α evolve [3]. Therefore, not only does a single point experience multiple thermal gyrations between the Liquid-Solid transformation temperature, but also experiences multiple thermal cycles through the Solid-Solid transformation temperature ($\beta \leftrightarrow \alpha + \beta$). In AM, depending on applied parameters, it has been shown that the melting of one layer can cause the re-melting of about 5 layers below it [12, 13]. Thus, with the multiple thermal excursions across different temperatures, with varying thermal rates in a constantly evolving part geometry, it is apparent that different locations within an AM build will experience different thermal+mechanical signatures. And so, this leads us to the underlying need to comprehend the physical sciences and physical metallurgy of metal alloys under AM processing conditions.

Extensive fundamental and applied research had been done to accelerate the adoption of AM of Ti-6Al-4V (which is the alloy in study in the current research). A quick literature review by Web of Science shows there are more than 200+ articles related to this topic, starting with early work by Kobryn and Semiatin [14] and Kelly and Kempe [15, 16]. One of the emerging requirements for qualification of AM components is to understand the spatial and temporal heterogeneity of defects and microstructures that form within a complex geometry for a given processing methodology [17, 18]. As a starting point, let us consider the role of thermal gyrations. Raplee et al. showed that thermal gyrations, defined as repeated heating and cooling, are often complex depending on the geometry and the raster characteristics [19]. Shown in Figure 1.1(a) is the measured IR intensity at different locations of a Ti6Al4V build as a function of raster length. In this data, the red curve cools slower since it experiences rapid reversals due to shorter scan lengths. The blue curve although has high peak temperature it cools faster due to long raster length. The inset shows the extraction of decay rate (t_o) in a 25 x 25 pixels area. Locations with a long raster length show a large variation in temperature and a monotonous cooling to ambient temperature. Whereas the

locations with shorter raster length, with shallow temperature gradients, experienced many repeated heating and cooling cycles within a short duration. The map confirms that even within a small region, thermal conditions vary drastically, and this is bound to induce cyclic variations in thermal gradients and cooling rate. At the same time, Babu et al. found that $\alpha \leftrightarrow \beta$ phase transformations during on-heating and on-cooling [Figure 1.1\(b\)](#) always lagged behind the calculated phase fraction, even under slow heating and cooling [\[20\]](#). In addition, Sridharan et al. have shown that repeated heating and cooling above β -transus may lead to the changes in crystallographic texture of α -phase [\[21\]](#).

The above spatial and temporal changes in thermal gradients are expected to induce stresses above and below the yield stress of the phases, thereby leading to plastic instabilities [\[2\]](#). The plastic instabilities we refer to in our study is the imbalance in alternating compressive and tensile stress, due to large fluctuating thermal gradients, leading to build-up of localized plastic strains. Plastic straining at high temperatures are expected to change relative phase fractions and also the constitutive properties [\[22, 23\]](#). Although the role of thermal signatures can be rationalized based on nucleation and growth of the product phase from the parent phase under non-isothermal conditions, all the above work have not considered the role of thermo-mechanical gyrations and therefore form the motivation behind the current research. In general, fluctuating thermo-mechanical gradients can change the local solid/solid phase transformations in metals and alloys, which in turn can change the local constitutive properties leading to the evolution of plastic strain gradients [\[24\]](#). The current work pertains to the history-dependent dynamic interactions of phase transformations and deformation characteristics.

Aim of the study: The current research focuses on studying the solid/solid local thermodynamic equilibrium kinetics between two phases when subject to complex and

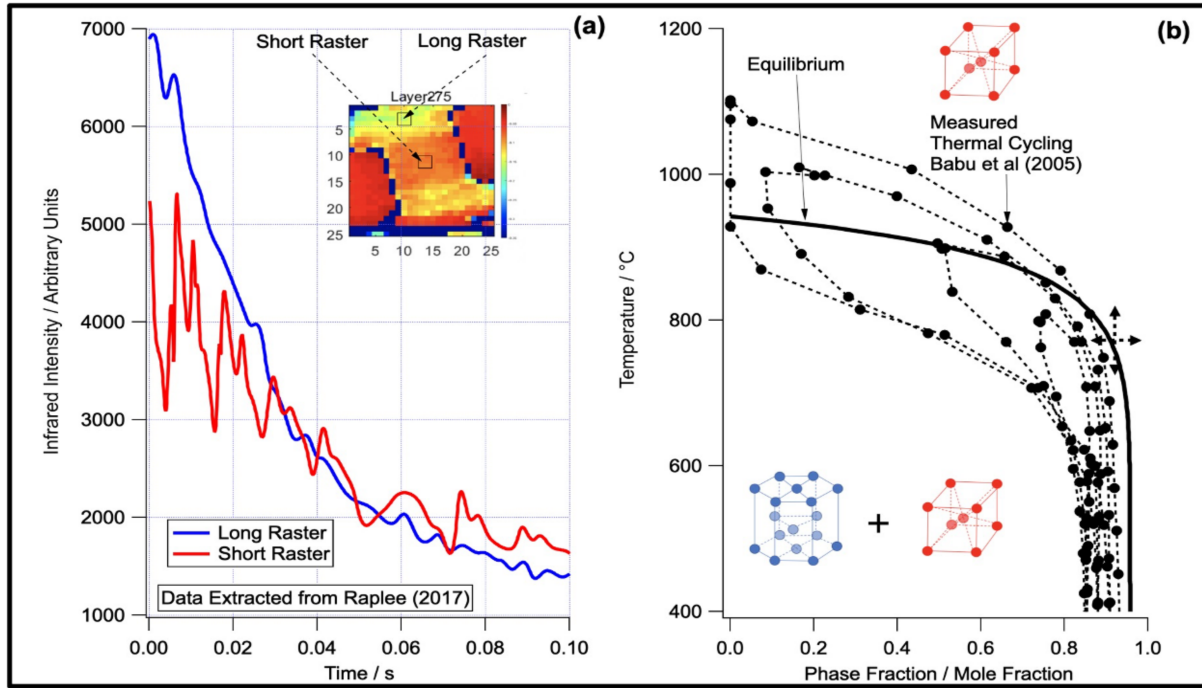


Figure 1.1: (a) Typical IR signature in two locations (within a 25 X 25 Pixel IR image) which is subjected to long- and short-laser raster. (b) Comparison of calculated equilibrium phase fraction of α phase in Ti6Al4V alloy with measured phase fraction using in-situ time-resolved X-ray diffraction shows that the kinetics on cooling and heating always lags behind the equilibrium.

fluctuating thermo-mechanical gyrations in an AM Ti6Al4V. This particular alloy is chosen in specific because of the extensive research that has been conducted on conventional manufacturing of Ti6Al4V. With a plethora of knowledge base and fundamentals to refer to, our goal is to assess the physically metallurgy of Ti6Al4V processed via Additive Manufacturing. A short brief of each of the chapters covered in this research is mentioned below.

- Chapter 2: An overview of the published literature on Metal Additive Manufacturing followed by a brief on Titanium Metallurgy. The overall goal of the study is outlined, highlighting the unknowns in the field of AM of the Ti6Al4V system, introduction to the problem statements and an outline of the hypothesis followed by a short section on the tools used to interpret the alloy behavior.
- Chapter 3: The preliminary ex-situ study of a Ti6Al4V cube manufactured by E-PBF with three distinct scan strategies is examined. A Semi-Analytical heat transfer model is used to establish correlations between the α and β phase features.
- Chapter 4: Complex thermo-mechanical reversals are imposed onto an EBM fabricated Ti6Al4V alloy. Preliminary ex-situ characterization of these samples indicated the occurrence of a dynamic phase transformation with an increases β phase stability concurrent with an overall flow softening. A study of the strain partitioning behavior is examined by in-situ thermo-mechanical reversals at the neutron beamline.
- Chapter 5: An in-depth study of the α/β interface of the ex-situ thermo-mechanically cycled samples is done with nano-scale Atom Probe analysis. The concentration profiles of Al and V across the interface suggested the feasibility of a reconstructive type of phase transformation rather than displacive, even at temperatures where no phase

transformation is expected. These results were further validated with computational thermodynamics using ThermoCalc[®].

- Chapter 6: A time-resolved study of the partitioning and accumulation of plastic strains between the α and β phases is studied via in-situ high energy X-ray diffraction experiments conducted at the CHESS beamline. FWHM analysis of the indicated an increasing effect in the accumulation of plastic strains across the Basal, Prismatic and Pyramidal planes with a higher impact tracked in the Basal planes of the α phase. Dynamic transformations of $\alpha \rightarrow \beta$ were further investigated by a quantitative analysis of the interface solute concentrations (Al and V) via Atom Probe Tomography, which indicated a decreased Vanadium concentration across the β phase. These results were the evaluated with a Thermodynamic Diffusion model, DICTRA[®] to validate the thermodynamic equilibrium kinetics of the α/β interface when under complex thermo-mechanical reversals.

CHAPTER 2

Literature Review

This chapter will review the different process in metal Additive Manufacturing, the impact of temperature reversals and large and fluctuating thermal gradients (G) leading to varying interface velocities (R). An overview of Titanium metallurgy and the reported literature on the phase kinetics associated with thermo-mechanical behavior of Titanium alloys will be discussed in this chapter.

2.1 A brief on Additive Manufacturing

2.1.1 *Additive Manufacturing Processes*

Additive Manufacturing (AM) has been gaining wide-spread popularity in current research field of material science and manufacturing due to the ability to fabricate a variety of complex and near-net shapes by printing a part bottom-up one layer at a time. The feasibility to implement a broad range of materials selection (metals alloys, ceramics, polymers, composites), and capabilities to mend repairs in complex parts, that would have otherwise been a challenge, lay the foundation for many research opportunities in AM. Current day advances in AM machines have the feasibility to deploy in-situ monitoring devices during AM processing and external in-situ experiments have paved the way for a addressing the

complex physical interactions during AM that further aid in computational models, neural networks and data analytics [25–29]. A classic example is the tracking of melt-pool geometry under varying energy densities and tracking the phenomena of pore/defect generation and Liquid/Solid interface velocities [30]. The end goal of the AM is to consolidate the feed stock into a solid part with minimal to zero post-processing steps. It has become quite clear that achieving a wholesome part with isotropic properties and near-net shapes is challenging. More recently, researchers have developed hybrid systems, such as the MAZAK systems, that combines additive manufacturing with simultaneous machining to fabricate parts to precise dimensions [31, 32]. As per ASTM F42 standard, there are 4 process out of the 7 AM processes that pertain specifically to Metal AM [10, 33], and are briefly discussed below.

(1) Powder Bed Fusion (PBF): Powder Bed Systems utilize a focused energy beam, a laser or an electron beam, to melt a specific regime as per a CAD model that is fed into the system. A layer of powder is then raked, the beam rasters across the part and melts the layer and this process continues until the part is complete. The build volume of these systems is quite low (around 0.03 m^3) although a large amount of powder feed is incorporated as the build proceeds [33]. PBF’s resolution is a direct function of the beam diameters (L-PBF: 20-100 μm and E-PBF: 100-200 μm), layer thickness, powder particle size and heat source power (L-PBF: 200-500W and E-PBF: 1000-6000W). Thus, L-PBF systems render a Ra surface roughness of 5-10 μm whereas, E-PBF systems range between 20-25 μm .

Electron Beam Melting: The Electron Beam Melting (EBM) uses a focused electron beam as the source of melting and so must be carried under vacuum, usually maintained at about $1 \times 10^{-5} \text{ mBar}$. The 2 hoppers on either side of the machine are filled with powders and a rake is used to spread an even layer of powder across the substrate. EBM process are unique in that the substrate plate is maintained at a desired temperature (eg: Ti6Al4V builds: 475-660°C and for Ni-based alloys: $\sim 1000^\circ\text{C}$) throughout the build. This is significant especially

for the first few layers as sharp temperature gradients ($\sim 10^7 \text{K/m}$) can cause distortion (as in L-PBF systems). Thus, the substrate, which renders the part mechanical support while being built, also provides a thermal path to dissipate heat [10]. The part along with the sintered powder is then taken to a powder recovery system, where the excess powders are blown off. EBM processes are straightforward and since the process takes place under vacuum, it prevents any form of oxidation from affecting the build. Although, as mentioned earlier the build volume is quite low for the EBM systems, they offer the capability of fabricating parts with high precision and complexity. The EBM ARCAM systems have an inbuilt Near-Infrared camera system that enables the in-situ tracking of melt and rake phenomenon's and are also used to data analysis on defects structures and temperature distributions in AM parts [34].

(2) Direct Energy Deposition (DED): The DED process is one in which a focused energy beam, either a laser beam or an electron beam, creates a melt pool, into which a feedstock, in the form of wire or powder, is fed in. One of the advantages of the DED process is the fabrication of large size components, since the feedstock is concentrated at the molten region. Although, there is a compromise in the surface finish of the part, combined with some post-processing, this method of AM can be a powerful technique for repairing damage [35].

(3) Binder Jet: The Binder jet process is unique in such that each layer does not experience the melting of powders during fabrication as in PBF and DED systems. In this process, a layer of powder is raked over followed by the deposition of a binder according to a CAD model, that binds the powders together. The consolidated part is then sintered. A big advantage of this system is the infiltration of a secondary metal to enhance the quality of the part, for instance, the infiltration of bronze into a stainless-steel part to achieve a final

density of 95% [36–38]. One of the major issues with this method is the control of porosity and shrinkage during sintering.

(4) Sheet Lamination: Sheet Lamination is another method of AM that stands out from others in such that it is a solid-state welding process in which a metallurgical bonding is achieved by the sliding of one sheet against the other. The Ultrasonic AM is one of the most popular methods used, joining of layers is achieved by applying ultrasonic vibrations with a sonotrode (at 20KHz) and an applied normal loading [39–41]. The high strain rate ($\sim 10^3 \text{ s}^{-1}$) adiabatic heating, with temperatures as high as 380 °C across the interface at the deformation induced zone ($\sim 20\mu\text{m}$ in depth), promotes rapid recrystallization of the deformed grains, leading to a bond. Overall temperature of the build is low ($\sim 25^\circ\text{C}$) and is advantageous in dissimilar weld joints and embedding of actuators and sensors in parts [42, 43].

2.1.2 *Complex spatial and temporal transients of temperature reversals in AM*

One of the great advantages of AM is the flexibility to control processing parameters, thereby rendering the desired outcome of solidification texture (equiaxed versus columnar) and microstructural features (such as crystallographic texture) of a system. Thus, optimized parts can be fabricated via AM by tailoring process parameters to pertain to a specific application for that part. As with traditional manufacturing processes, like casting and welding, defects and part quality are a common concern in metal AM. Parameters such as the scan strategy, process temperatures, beam conditions, feedstock, build chamber atmosphere and many other inputs influence the occurrence and quantity of defects. But the metallurgy of AM parts primarily depends on the feedstock chemistry and thermal+mechanical history

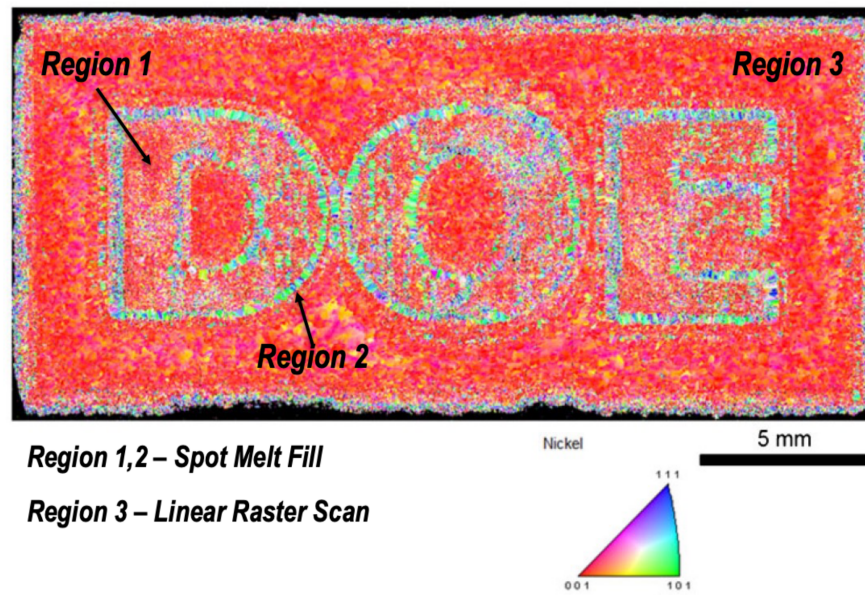
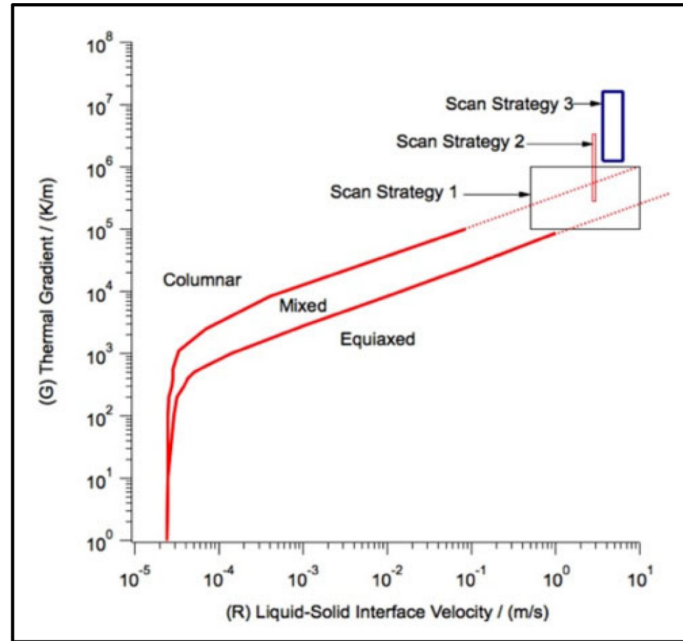


Figure 2.1: (Top) CET curve predicting the solidification structure of the 3 scan regions across the DOE build [1]; (Bottom) Site-specific control of solidification texture achieved by alternating the AM melt scan path between a linear raster to a spot-fill pattern. [1]

of the part during fabrication. Furthermore, heat source factors such as beam speed and power contribute to the assessment of the solidification kinetics of the alloy in AM.

The primary weld parameters that are important in determining the microstructure and grain morphology are the temperature gradient (G (K/m)), liquid/solid interface velocity (R (m/s)), cooling rates (dT/ds) and undercooling (ΔT). The directionality and sign of the temperature gradient influences the growth and solidification at the liquid/solid interface [44, 45]. The temperature gradient (G) and interface velocities (R) are important also in the combined form, where $G.R$ indicates the cooling rates (K/s) and G/R gives information on the solidification substructure and morphology respectively. And thus, higher thermal gradients (10^6 - 10^8 K/m) with lower interface velocities (10^{-3} - 10^{-3} m/s) render more columnar dendritic type morphologies whereas, shallow thermal gradients (10^2 - 10^2 K/m) with higher interface velocities (10^{-1} - 10^1 m/s) lead to more equiaxed grain morphologies. Commonly known as the Columnar-to-Equiaxed (CET) model, as seen in Figure 2.1 (CET of IN718 alloy [1]), initially developed by Hunt for casting processes to predict the competition between columnar and equiaxed grain growth, many computational models have since been developed to predict the competing grain growth structures during solidification in AM [46–48].

However, unlike welding, during AM, a localized region is subject to multiple thermal excursions of melt cycles, ~ 5 -8 cycles between the liquid/solid temperatures and ~ 30 -40 cycles between solid/solid temperatures. Thus, complex thermal interactions happen over a 500-layer (25mm, taking into account a layer height of 50 μm) part. A classic example of site-specific control of solidification texture was achieved by alternating the AM melt scan path between a linear raster to a spot-fill pattern. Shown in Figure 2.1, is a block E-PBF printed with a linear raster scan (Region 3 printed with Scan Strategy 3) within which the letters DOE are printed with a spot melt pattern (Region 1 & 2 - printed with Scan Strategy

1 & 2 respectively, differing in spot fill patterns) [1]. By doing so, the letter's DOE were outlined with highly misoriented grains, as seen from the IPF map shown in Figure 2.1, while the bulk was dominated by highly oriented columnar [001] grains along the build direction. This study indicates that control over the desired texture, morphology and microstructure within a build is controlled by spatial and temporal signatures of T, G and V evolving within the build. Several other studies have shown the influence of varying deposition energy's and scan strategies in the outcome of the microstructures evolving as a function of build height [49–57].

2.1.3 *Overview of macro stresses and strains*

One of the critical issues in welding and AM is the evolution of residual stress distribution. Residual stress can build up in a part during welding due to the non-uniform accumulation of plastic strains. Majority of these micro plastic strains are brought up by thermal stress generated from macro-scale temperature gradients during thermal cycling, localized changes in thermal expansion coefficients of the different phases in the system and crystallographic/misfit strains evolving from liquid-solid and solid-solid phase transformations.

A detailed explanation of the build-up of residual stress during welding is explained by Masubuchi [2]. A schematic of a bead-on weld and the emerging temperature and stress profiles are shown in Figure 2.2. Ahead of the arc at section A-A, the temperature changes as well as the stress is at zero. At the arc region, there is a steep temperature distribution. Since the molten metal does not carry any load, the stress is a zero at the center, becomes compressive as metal tends to expand, while the region next to it, goes into tension. At section C-C, the temperature has cooled off a little, as seen in the temperature profile. The once molten metal now starts to shrink on cooling, inducing tensile stresses with the adjacent region in compression. At section D-D, where the weld zone is cooled off, the temperature

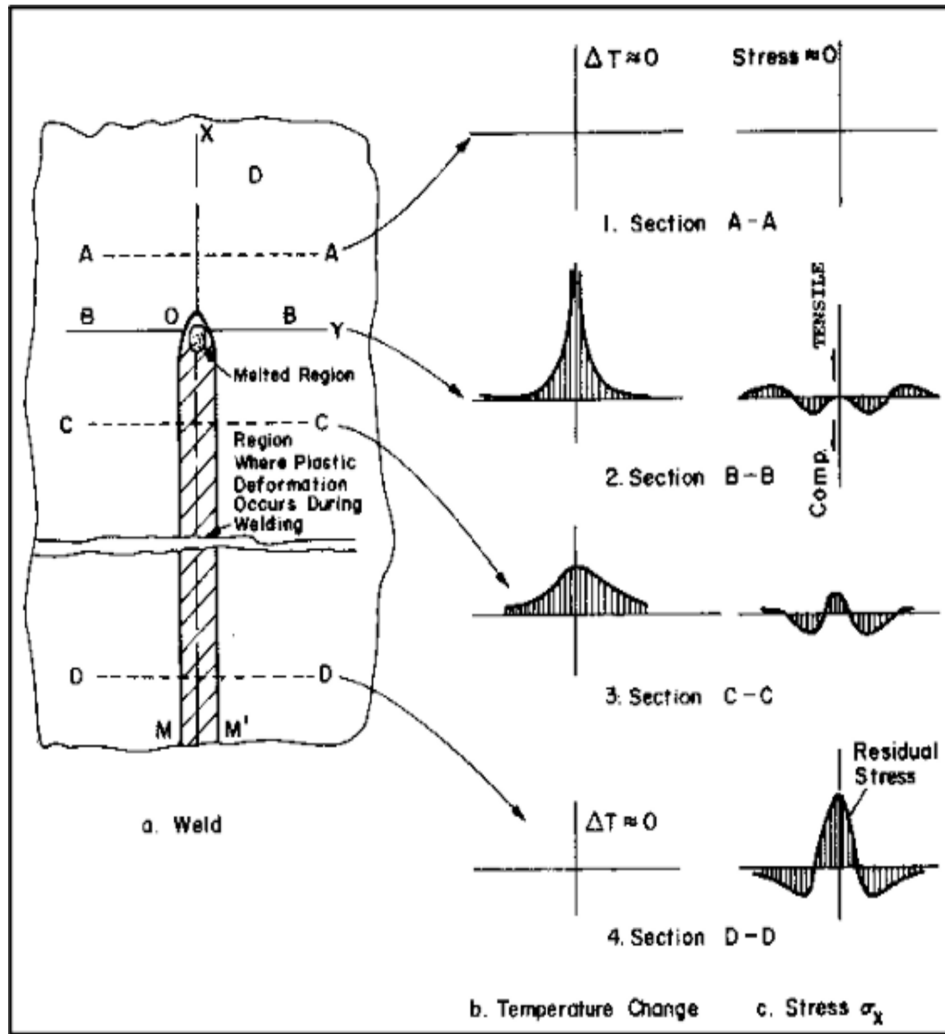


Figure 2.2: Residual stress profile and temperature profile during a single bead-on weld [2].

distribution profile becomes a zero, whereas the center of the weld is left behind with tensile residual stress surrounded by compressive residual stress. This schematic understanding of the evolution of residual stress is for a single bead on plate.

Mukherjee et al. investigated the evolution of stresses and strains across In718 and Ti6Al4V builds using a 3-dimensional transient heat transfer model with fluid flow to model the temperature, residual stress and distortion in AM using the DED process [58, 59]. Their simulation results shows an anisotropy in the residual stress distribution within 10 layers of the build across the x, y and z directions, where the transverse direction (y-direction) the stresses alternatively change from compressive (max stress:-500 MPa) to tensile (max stress:600 MPa) through the height of the build. Whereas, along the build direction, compressive stresses (max stress:-300 MPa) remain in the center of the build with tensile stress (max stress:500 MPa) along the edges of the build. Residual stresses also arise due to the thermal mismatch between materials of the start plate and the build. Since EBM builds have the unique capability of a pre-heat step, they are known to have lower residual stresses than the L-PBF builds. Sochalski et al. compared the residual stresses in IN718 from the EBM process and the L-PBF process using neutrons and showed the occurrence of tensile residual stresses in the center for EBM builds whereas for the L-PBF builds were mostly compressive in nature [60]. Although residual stresses have a larger impact on the macro scale in the part causing issues such as warping and distortion, the micron-scale effects of localised strained regions and their impact on the solidification evolution are yet to be studied.

2.1.4 *Plastic instabilities during AM*

However, in AM, with repeated thermal cycling in a evolving geometry, it is plausible that localized alternating compressive and tensile stresses begin to accumulate, leading to

a complex *plastic instability* at the interface as well as microstructural degradation at the interface. Plastic instability can be best defined in a sample under uni-axial tension by the condition of $dP=0$ [61]. When a metal undergoes strain hardening, the stress (load carrying capacity) of the specimen increases as deformation increases. At the same time, in opposition to this strain hardening, a gradual decrease in the cross-sectional area of the specimen occurs as the specimen elongates. Thus, necking or localised deformation occurs when the increase in stress due to the decrease in the cross-sectional area of the specimen is greater than the stress due to strain hardening. This condition of instability leads to local deformation (necking) leading to fracture. The plastic instabilities we allude to in our research, primarily refers to the imbalance in compressive and tensile stresses imposed locally in a phase, due to the large and fluctuating thermal gradients experienced during AM processes, causing localised plastic deformation. These local regions of plastic deformation can influence the texture of phases (for example, variant selection of the α phase on cooling [62]), phase transformation kinetics ($\beta \rightleftharpoons \alpha$ in Titanium alloys) and defect (crack tendency and pore formations) generation within a part.

Non-uniform plastic strain evolution during repeated thermal cycling is caused due to thermal stresses brought about by macro scale thermal gradients, local changes in thermal expansion coefficients, crystallographic misfits between phases and constitutive stress-strain properties[63]. Lee et al. have demonstrated the influence of a localised stress gradient on the cracking susceptibility during the E-PBF of Mar247 alloy [64]. Their simulation results indicate that when a sufficient temperature ($\sim 1500\text{K}$) exists concomitantly with a tensile stress range ($\sim 300\text{MPa}$), cracking is prone to occur. On the other hand, where temperature profiles exist with dominant compressive stresses (~ -30 to -60 MPa), cracking cannot occur even though there exists a wide susceptible temperature range. These accumulated plastic strains can indeed impact the Solid/Solid phase transformations that occur during the

multiple thermal fluctuations. Foster et al. attributed the heterogeneities in hardness observed in In718 builds due to accumulated plastic strains that occur due to thermal stress evolution during processing [28]. McNeil et al. observed a defect-free regions of about 100 μ m around large pores [26]. The spatial and temporal gradients tracked from via in-situ infrared signatures were related to thermo-mechanical conditions. These studies thus put forth a different perspective of the AM process that differentiates it from conventional manufacturing, whereby the metallurgical features in an AM part are primarily dictated by an overall interaction of thermo-mechanical-metallurgical drivers due to the layer-by-layer build up of a part experiencing fluctuating signatures.

2.2 Ti6Al4V alloy Metallurgy

2.2.1 Overview of α and β phases in Ti6Al4V

Titanium alloys have 2 primary phases, a high temperature Body Centered Cubic (BCC), β phase and a Hexagonal Close Packed (HCP), α phase, as shown in Figure 2.3(a). It is a combination of these two phases, that renders $\alpha+\beta$ titanium alloys superior mechanical properties through a range of temperatures. The HCP α phase has a lattice constant of $a = 2.95 \text{ \AA}$ and $c = 4.68 \text{ \AA}$, which then gives a c/a ratio of 1.587, which is smaller than the ideal c/a ratio of 1.633 for HCP structures. The implications of this low c/a ratio is seen in its deformation behavior, where this reduced c/a ratio leads to increased packing density within the prismatic planes. Thus, favouring prismatic slip over basal slip in the HCP system. The shaded areas (in Figure 2.3(a)) mark the 3 close packed lattice planes of the HCP α system, namely, the (0001) basal plane, one of the three $\{10\bar{1}0\}$ prismatic plane and one of the six $\{10\bar{1}1\}$ pyramidal planes. The marked co-ordinates of a_1 , a_2 and a_3 are the closed packed

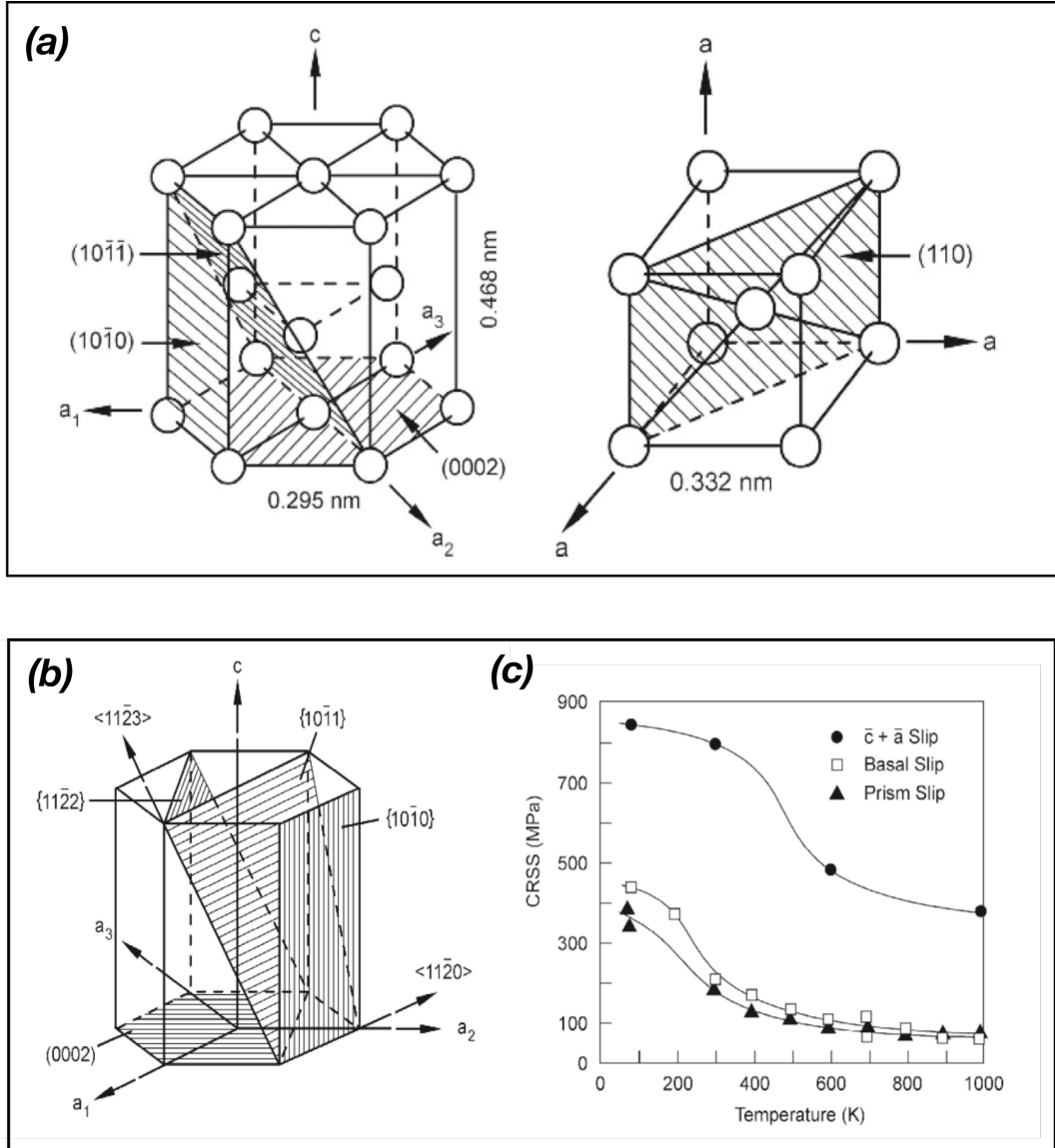


Figure 2.3: (a) HCP α phase and BCC β crystal structure [3]; (b) Common slip direction and planes in the HCP α system [3]; (c) CRSS of the 3 common slip systems in the α phase with temperature [3]

$\langle 11\bar{2}0 \rangle$ direction. The BCC crystal, has 6 $\{110\}$ family of close packed lattice planes and 4 $\langle 111 \rangle$ closed packed directions with a lattice constant of $a = 3.32 \text{ \AA}$ at 900°C [3].

Burger's Orientation Relationship: An allotropic transformation from β phase to the α phase occurs at the β -transus temperature, which is about 1000°C for Ti6Al4V system. This temperature is highly dependent on the interstitial and substitutional alloying elements present in the specific alloy. The transformation of the high temperature BCC β phase to the HCP α phase occurs martensitically or diffusion controlled depending on the rate of cooling and alloy composition. Transformation follows a specific Burgers Orientation (BO) relationship where the $(110)\beta \parallel (0001)\alpha$ and the $[1\bar{1}1]\beta \parallel [11\bar{2}0]\alpha$. According to this BO relationship, α can form 12 different variants from a single β grain. Conversely, the β phase can form 6 variants from an α grain.

Microstructural Features: On heating above the $\beta_{transus}$ temperature (990°C), the $\alpha+\beta$ transforms to single phase BCC β . On cooling below the $\beta_{transus}$ temperature, the β phase transforms into a variety of α morphologies depending on the cooling rates and subsequent solute concentrations. On very fast cooling rates, of about $\sim 410 \text{ K/s}$, β decomposes via a diffusion-less pathway to martensitic α' [3, 65], as shown in Figure 2.4(a). The martensitic start temperature ranges between $600\text{--}850^\circ\text{C}$, and increases with increasing amounts of α stabilizers, such as aluminum and oxygen, and decreases with increasing β stabilizer content [66, 67]. The fast cooling rates during AM (in the order of 10^4 K/s), below the $\beta_{transus}$ temperature, martensitic α' forms. On further thermal cycles, the α' decomposes into $\alpha_{primary}+\beta$ [68]. Massive transformation of β to α_m phase occurs at moderate cooling rates and is composition invariant. Massive α_m have a blocky morphology and a heavily dislocated substructure.

On slower cooling rates ($\sim 20 \text{ K/s}$), a diffusional transformation of $\beta \rightarrow \alpha+\beta$ occurs. The first α to form on cooling below $\beta_{transus}$ is the allotriomorphic or $\alpha_{grain-boundary}$ that nucleate

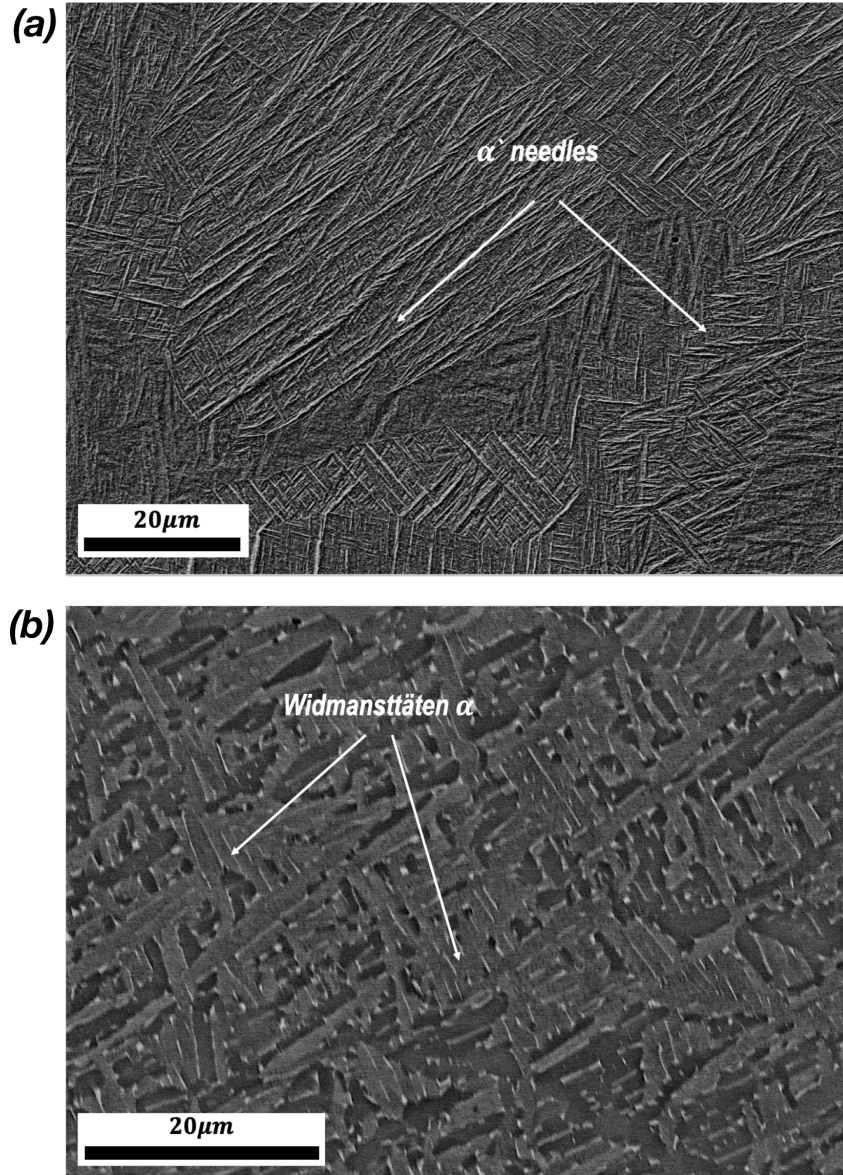


Figure 2.4: (a) Martensitic α' needles in a Ti6Al4V lattice cube processed via SLM; (b) Widmanstätten α separated by β ribs (white regions) in a Ti6Al4V cube sample fabricated via E-PBF.

on the grain boundaries of β grains. On further cooling, two types of $\alpha_{primary}$ morphology form – a colony α and a basket-weave α or Widmanstätten α , shown in Figure 2.4(b). α -colony laths grow from the α -grain boundary on further undercooling. To minimize the overall elastic strains, the new α plates nucleating by "point" contact on the broad face of an existing α plate tend to grow nearly perpendicular to that plate. This selective nucleation and growth mechanism in combination with the smaller number of α plates within the colonies leads to a characteristic microstructure called "basket weave" structure. With slower cooling rates and growing undercooling, there is more driving force for the α to form from the remaining β . Due to multiple thermal cycles and prolonged hold temperatures during E-PBF, the typical microstructure of Ti6Al4V consists of coarse basket-weave α [54, 69, 70].

Impact of Alloying elements: Titanium alloys can be classified based on the proportion of the 2 phases, namely (i) $\alpha+\beta$ alloys, (ii) α alloys and (iii) β alloys. Alloying elements play a vital role in the outcome of the alloy. Aluminum, and interstitial such as C, N and O are strong α stabilizers. These elements tend to increase the β transus temperature, enabling a larger α region. Elements such as V, Mo, Fe, Cr, Ni, Cu and H are β stabilizing elements. Diffusion of these alloying elements have a great impact on the outcome of the microstructure.

2.2.2 *Deformation mechanisms in α and β phases*

Deformation in Titanium alloys especially at low temperatures occurs mainly by twinning mechanisms and slip by dislocations. Slip in the closed packed planes of the HCP α phase consist of $\langle a \rangle$ and $\langle c+a \rangle$ type burgers vector and is shown in Figure 2.3(b). The common $\langle a \rangle$ type slip planes are the (0001) basal plane, the three $\{10\bar{1}0\}$ prismatic planes and the six $\{10\bar{1}1\}$ pyramidal planes with the $\langle 11\bar{2}0 \rangle$ closed packed direction. Among these there are a total of 12 slip systems. $\langle c+a \rangle$ type slip has also been observed in titanium

alloys along the $\langle 11\bar{2}3 \rangle$ direction and the $\{11\bar{2}2\}$ planes. The nature of the dislocations are found to be a mixture of edge and screw dislocations [71–73]. Due to the compatible α/β interface, it has been shown that basal and prismatic glide is more favored with dislocations being emitted from the α/β interface [74]. Activation of any slip in a phase is described by the critical resolved shear stress (CRSS) of the particular slip system. As seen from Figure 2.3, the CRSS in the α phase for the $\langle a \rangle$ type, basal and prismatic systems is orders of magnitude lower than the $\langle c+a \rangle$ type of slip. In general, $\langle c+a \rangle$ type slip across the second order pyramidal planes is rather difficult when compared to the lower CRSS of the $\langle a \rangle$ type slip across the prismatic and basal slip systems. Slip in the BCC phase occurs on $\{110\}$, $\{112\}$, $\{123\}$ family of planes with $\langle 111 \rangle$ direction, with a total of 48 slip systems [3].

Deformation mechanisms in the $\alpha+\beta$ titanium alloys tend to be more complex due to the interlocked and fine textured α lamellar colonies, separated by β ribs. This complex microstructure renders them beneficial for high strength applications, as the size of the α colony determines the effective slip length [75]. An in-situ TEM study on the deformation micro-mechanisms in Ti6Al4V has shown that dislocations are largely emitted from the α/β interfaces and glide along primarily the prismatic and basal slip planes [74, 76]. The β phase has also shown to contribute to easy slip transmission along specific slip systems through the α/β interfaces, according to the BO relationship between the two phases [77–79]. In some cases, these α/β interfaces are known to act as obstacles to dislocation motion, thus providing better mechanical properties [75, 80].

2.2.3 α/β Phase kinetics on thermo-mechanical processing

Conventionally cast α/β Titanium alloys usually have about 10 – 20% β phase with the rest balance being the α phase. Dynamic transformations during thermo-mechanical processing

in the $\alpha+\beta$ region has been of much interest in the titanium research community, since the occurrence of dynamic transformations $\beta\rightarrow\alpha$ acts as the primary source for flow softening during processing [22, 81, 82]. Titanium alloys, in specific, has been of much interest since it is one of the most difficult alloys to process. Especially in the $\alpha+\beta$ alloys, hot working temperature must be low, around 0.65 – 0.75 of the solidus temperature in order to control the microstructure making it attractive for application in the aerospace field [81]. At these low temperatures the flow stress of most titanium alloy is high, thereby narrowing the window of thermo-mechanical processing.

A brief literature on dynamic phase transformations during thermo-mechanical cycling and the influence on the interface stability of the α and β phase under various conditions of thermo-mechanical processing is summarized below. The thermo-mechanical processes discussed below consist of isothermal temperature holds followed by deformation (either hot compression or tension loads). These literature sources point to various debates on the phase transformation kinetics of $\alpha+\beta$ titanium alloys when subject to varying thermo-mechanical processes. Some researchers have argued that thermo-mechanical processing (isothermal hot deformation processes) results in an increase in the α phase fraction, whereas in other cases, an increase in the β phase fraction.

Increase in α phase stability: The effect of a strain induced phase transformation has been heavily studied in steels and is known to bring about grain refinement, which ultimately improves the strength of the alloy. Ali-Dehghan et al. studied the thermo-mechanical processing of a Ti6246 alloy, where they attributed work softening to the $\beta\rightarrow\alpha$ phase transformation during processing (an increase of the α phase fraction from 5% to 15%). They showed that a dynamic strain induced transformation occurred, where the increase in the deformation bands and accumulation of dislocations at β grain boundaries acts as potential nucleation sites for α [83]. He et al. also shows that the fraction of

the α phase in Ti-6Al-4V alloy noticeably increased by deformation during slow cooling post thermo-mechanical processing [84]. Guo et al. have shown similar trends on isothermal holds post-deformation of Ti-6Al-4V, a reverse transformation, $\beta \rightarrow \alpha$ takes place, the driving force being the difference in the Gibb's free energy between the two phases [85]. In general, a $\beta \rightarrow \alpha$ transformation occurs during and post thermo-mechanical deformation.

Increase in β phase stability: On the other hand, an increase in the β phase fraction during thermo-mechanical processing in α/β titanium alloys have also been reported, where a stress-induced or deformation-induced phase transformation leads to an increase in the β phase fraction. Koike et al. examined the $\alpha \rightarrow \beta$ transformation during the superplastic deformation of a Ti-Al-Fe alloy [86]. In their post-deformation analysis of the sample, they noticed an agglomeration of the β phase at regions perpendicular to the tensile axis and depleted at the parallel boundaries. During this uniaxial stress condition, boundaries parallel to the tensile axis are in a compressive state whereas those that are perpendicular to the axis are in a tensile state. As a result of this stress gradient, a difference in the chemical potentials of the vacancies causes a diffusional flow of atoms from compressive boundaries to the tensile boundaries. In their case, Fe being the fast-diffusing element and a β stabilizer, diffuses to the tensile boundaries.

Similarly, a study by Yang et al, showed an increase from 20% to 60% of β phase fraction with increasing strain to 1.2% in Ti6Al4V alloys subject to super plastic deformation at temperatures of 1123K [87]. They concluded that an increase in the β volume fraction is a process towards a thermodynamically stable state accelerated by deformation. In the work by Zhang et al., an increase in the superplastic elongation at temperatures between 700 °C and 800 °C in Ti-6Al-4V was partially attributed to the agglomeration of β phase along grain boundaries and subsequent strain induced phase transformation from the $\alpha \rightarrow \beta$ [88]. Guo et al. also indicated an increased β phase fraction in the deformed sample across

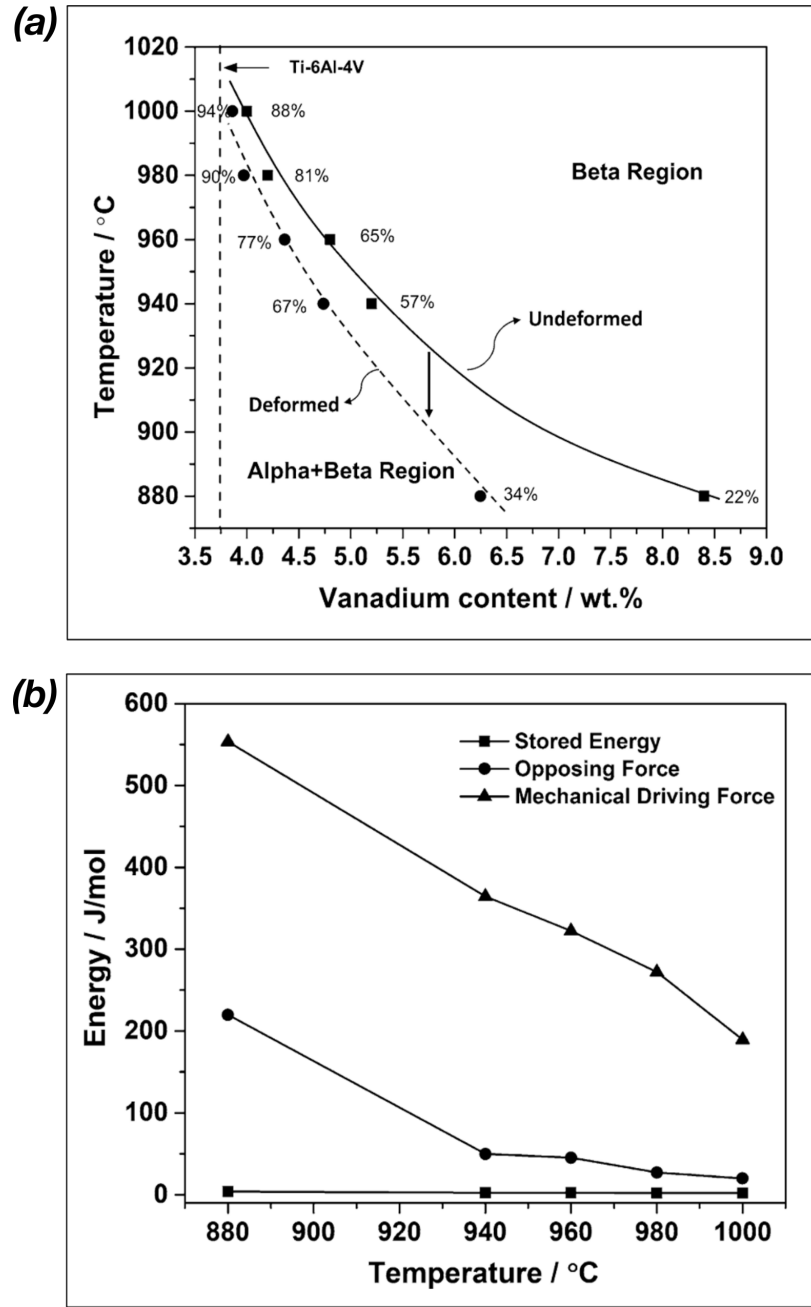


Figure 2.5: (a) An increased α phase fraction noticed in the deformed sample measured across temperatures between 880 °C and 1000 °C [4]; (b) Comparison of the stored energy, energy associated with opposing forces and mechanical work, showing that the energy from mechanical driving forces are orders higher than the opposing forces and stored energy [4].

varying temperatures as shown in Figure 2.5(a), where an increased beta fraction is marked by the decreased in the Vanadium concentration [4]. In a following study by Guo et al., they proposed that the flow softening due to dynamic transformation of $\alpha \rightarrow \beta$ subject to thermo-mechanical processing occurred by the displacive nucleation of β and deformation assisted diffusion, where defects and dislocations provided pathways for diffusion, i.e., pipe diffusion [82].

Super-plastic deformation studies on Ti6Al4V have shown that, (1) deformation increases the β phase fraction, (2) dislocation is observed to accumulate in the β phase, (3) agglomeration of the β phase between the α/α grain boundaries and (4) increase in the dislocation density at the α/β (heterogeneous) interface. In summary, a deformation induced or rather a stress-induced phase transformation of $\alpha \rightarrow \beta$ occurs, leading to an increase in the β volume fraction [22, 82, 87, 89–91].

Thermodynamics involved in the transformation kinetics: Stemming from the early studies of dynamic transformations of austenite to ferrite in Steels, thermodynamic models later indicted the occurrence of such transformation in Titanium alloys too [92]. The thermodynamics involved in the above-mentioned dynamic transformation during thermo-mechanical processing has been outlined by Guo et al., [4]. In their study, the *opposing* and *driving* forces for dynamic transformations are outlined based on the proposed theory of displacive type of transformation associate with a deformation-assisted diffusion. The 3 obstacles opposing dynamic transformations in Titanium include the overall Gibb’s free energy difference between the α and β phases (based on solution thermodynamics), the dilatation work (calculated with a dilatation strain of 0.17 [93]) and shear work involved in the displacive transformations (α to β involves a shear strain of 0.14 [94]). Secondly, the contribution of stored energy per unit volume associated with dislocation is calculated, based on the initial and final dislocation density, shear modulus (temperature dependent

term, GPa) and burgers vector ($b=2.95 \times 10^{-10}\text{m}$) [95]. Finally, the mechanical driving force, which is a combination of the stored energy, net flow softening (calculated by the difference in the critical stress of α and yield stress of β [96]) and heat dissipation. On comparing the stored energy, energy associated with opposing forces and mechanical work, they showed that the mechanical driving forces are orders higher than the opposing forces, shown in Figure 2.5(b) across temperatures ranging between 880°C and 1000°C. Thus, thermodynamically proving it possible for dynamic phase transformation of $\alpha \rightarrow \beta$ to occur.

Thus, in summary the phase stability and interface behavior of the α and β phase, in a two-phase Titanium system is highly dependent on the thermo-mechanical constraints it is subjected to. Research on the topic thus far have shown that localized strain fields, brought about by differences in the thermal expansion coefficients, macroscale thermal gradients, lattice strains due to phase transformations and defects due to deformation, act as either a barrier or enhancer for phase transformation to occur leading to flow softening. The above studies lay a foundation in terms of the α/β kinetics, for our study on the complex transients $\sum T(x, y, z, time, \sigma)$ under cyclic thermo-mechanical conditions, as experienced in AM processing.

Significance of TM processing in Titanium: With this background, it is clear that thermo-mechanical cycling has a significant impact on the resulting behavior of the phase stabilities and volume fractions. On deformation in the $\alpha+\beta$ region, Furuhashi et al. noticed that dynamic recovery took place between low angle α/α boundaries, whereas, some amount of dynamic recrystallization occurred between high angle α/α boundaries [97, 98]. Weiss et al. observed two different types of α lamella break-up during thermo-mechanical processing [99]. α lamella break-up occurred by the penetration of the β phase, either through α sub-boundaries or through the heavily sheared zones. Therefore, in the presence of high

dislocation densities, the rate of diffusion of the solute elements, Al and V, increases causing a break-up of these α laths into an equiaxed type grain [81].

The kinetics of phase transformations under rapidly evolving non-isothermal temperature and/or elastic/plastic strains is commonly referred to as ‘dynamic transformations. Guo et al. hypothesized that under these conditions, there is a dynamic balance of the Gibbs free energy of parent and product phase that is based on chemical composition, mechanical elastic energy, and stored energy based on defect density. They also stressed that under rapid deformation conditions, the localized temperature increase due to adiabatic heating also must be considered. This is indeed observed in the torsional deformation work performed by Babu et al. [23]. However, the published work has not considered the complete reversal of tensile and compressive plastic strains while under repeated heating and cooling in the two-phase field of Ti6Al4V, relevant to AM. The above theories of phase transformations in titanium alloys lay a strong base for investigating the spatial and temporal transients of thermo-mechanical fluctuations that is embarked in this research.

2.3 Scientific and Technical Approach

2.3.1 *Underlying Problem Statement*

Additive Manufacturing is a technology that combines many aspects of welding metallurgy, casting, and thermo-mechanical processes. As a result, it is a complicated process that is heavily reliant on the processing parameters and material characteristics, as detailed in the preceding sections. The implication of the scan strategy is one approach to illustrate the complexity of AM, where various scan methods cause a difference in the temperature distribution throughout a layer, which is constantly evolving as layers are added. This demonstrates that process parameters has a substantial influence on evolution of spatial and

temporal transients, $\sum T(x, y, z, time, \sigma)$ within the part during processing. Not only do these transients play an important role in dictating the solidification structure, distortion and defect generation in the part, literature has shown that these transients also play a vital role on the micro-level mechanisms, such as phase transformations and preferred localized textures. As a result, steady-state conditions, as assumed in conventional processes, are not strictly true for AM.

Large temperature gradients and frequent reversals of the sign on the gradient vectors (G_x, G_y, G_z) during AM processing, can impact the decomposition of the product to parent phase. For example, the interface velocity ($v_{interface}$) between two phases can be calculated based on the balance between the concentration of solutes in either phase and the diffusivity of the solute atoms [100].

$$(C_i^{P_1P_2} - C_i^{P_2P_1})v_{interface} = -D_i^{P_1}\frac{dc_i}{dx} - D_i^{P_2}\frac{dc_i}{dx}$$

In the above equation $C_i^{P_1P_2}$ is the interface concentration of solute " i " in phase P_1 and $C_i^{P_2P_1}$ is the interface concentration of solute " i " in phase P_2 . Similarly, $D_i^{P_1}$ and $D_i^{P_2}$ are the diffusivities of solute " i " in phases P_1 and P_2 respectively. Due to the rapid cooling and large differences in the diffusivity, the equality represented above may break down and induce constrained equilibrium conditions. But this equation holds good under isothermal conditions, which do not exist in AM, due to the large and frequent reversals of temperature gradients and thermal gyrations. For instance, Sridharan et al. reported a higher Vanadium partitioning (25 at%) to the β phase in E-PBF and L-DED builds, when compared to the Vanadium partitioning (18 at %) measured by thermodynamic models. They attributed these discrepancies to the $\alpha \leftrightarrow \beta$ transformations occurring at temperatures below the transformation temperature ($\beta_{transus}$), therefore resulting in an increased Vanadium in β [101]. The phase transformations that occur during the AM

of Ti6Al4V has also probed many questions on the martensitic start and finish (M_s and M_f) temperatures during the β decomposition on cooling and many have theorized these uncertainties based on the thermal profile and thermal gyrations at locations along and across the build [16, 21, 68, 102–105]. Similarly, Kirka et al. reported a microstructural gradient in the as-built state of an Inconel 718 alloy along the build direction. These variations are interpreted based on the different thermal signatures experienced in the build at different locations from the bottom [106–110]. Similarly, almost 200+ articles (as shown in the network plot in Figure 2.6) have been published that have identified microstructural gradients, variations in hardness, and defect formation in diverse alloy systems and linked them to temporal temperature transients and thermal gyrations encountered during AM processes.

It is well understood that non-uniform temperature distributions or rather significant thermal gradients result in the accumulation of plastic strains, and therefore there is a need to rationalize these heterogeneities in terms of *thermo-mechanical* boundary conditions [111]. The coupled impact of thermal + mechanical fluctuations during AM processing conditions have yet to be explored and forms the overarching goal of the study. Although much effort has advanced in the in-situ tracking of spatial and temporal signatures during AM processing, the above studies have highlighted the need for a deeper understanding of process-structure-properties (PSP) of AM engineered alloys [26–28, 112, 113]. In AM, where thermal gradients range between 10^3 K/m to about 10^7 K/m, coupled with fluctuating thermal gyrations $\sum (x, y, z, time)$, result in a spread of interface velocities ranging from 0 – 1 m/s within the build. Thus, it is key to understand the physical science underpinning the interplay of these sub-micron scale interface stability's (Liquid-Solid and Solid-Solid), to macro-scale fluctuations of the thermo-mechanical boundary conditions.

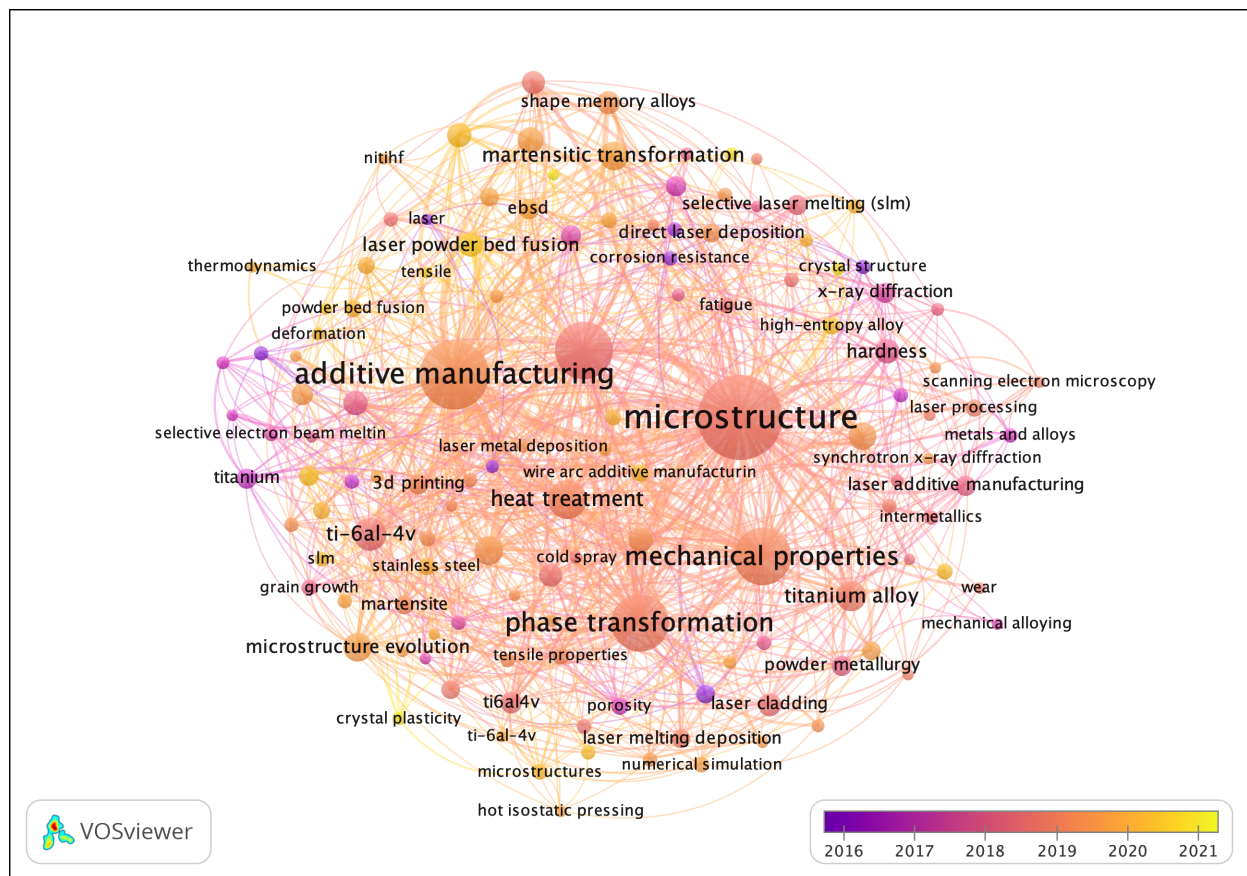


Figure 2.6: Network plot indicating the inter-connectivity of articles published in the Metal Additive domain, focusing in large on the microstructure, mechanical properties and phase transformations in different alloy system fabricated via varying Additive manufacturing processes, during the past 5 years.

2.3.2 *Hypothesis for the study*

When a two-phase alloy is subjected to fluctuating thermal cycles, one of the phases will tend to expand or contract relative to the other, owing to the differences in their thermal expansion co-efficient and young's moduli at different temperatures [111]. Plastic deformation sets to accommodate the differences in thermal expansion, when the thermal stresses in the phases are higher than the yield stress. As a result, multiple locations across a layer of the build will undergo cyclic thermal stresses above and below the flow stress [59]. As a result, an instability condition arises leading to a build-up of localized plastic strain gradients throughout the build. Residual stresses within the welded region can arise due to many factors, such as, differences in thermal expansion coefficients of different phases in an alloy, thermal stresses caused by macro-scale temperature gradients, crystallographic misfit strains, transformation strains and constitutive stress-strain properties. For instance, Babu et al. evaluated the role of role of thermal gradients and their reversals of plastic strain gradients (compressive and tensile) in two iron alloys containing varying fractions of ferrite (BCC crystal structure) and Cr_{23}C_6 precipitates, with minor differences in the initial microstructures [114]. The resultant hysteresis stress-strain plot revealed two different behaviors, with the strongest alloy exhibiting minimal softening but premature cracking and the softer alloy exhibiting significant softening but delayed failure. This behavior was associated with the ferrite/ Cr_{23}C_6 interface characteristics leading to the preferential generation of dislocation within grains followed by phenomenon's of crack initiation and recovery, during thermo-mechanical reversals [115].

The uneven temperature distribution produced during welding gives rise to incompatible strains which in turn result in self- equilibrating residual stresses that remain in the structure after it has cooled down to ambient temperature. The 3 bar analogy is one way to explain

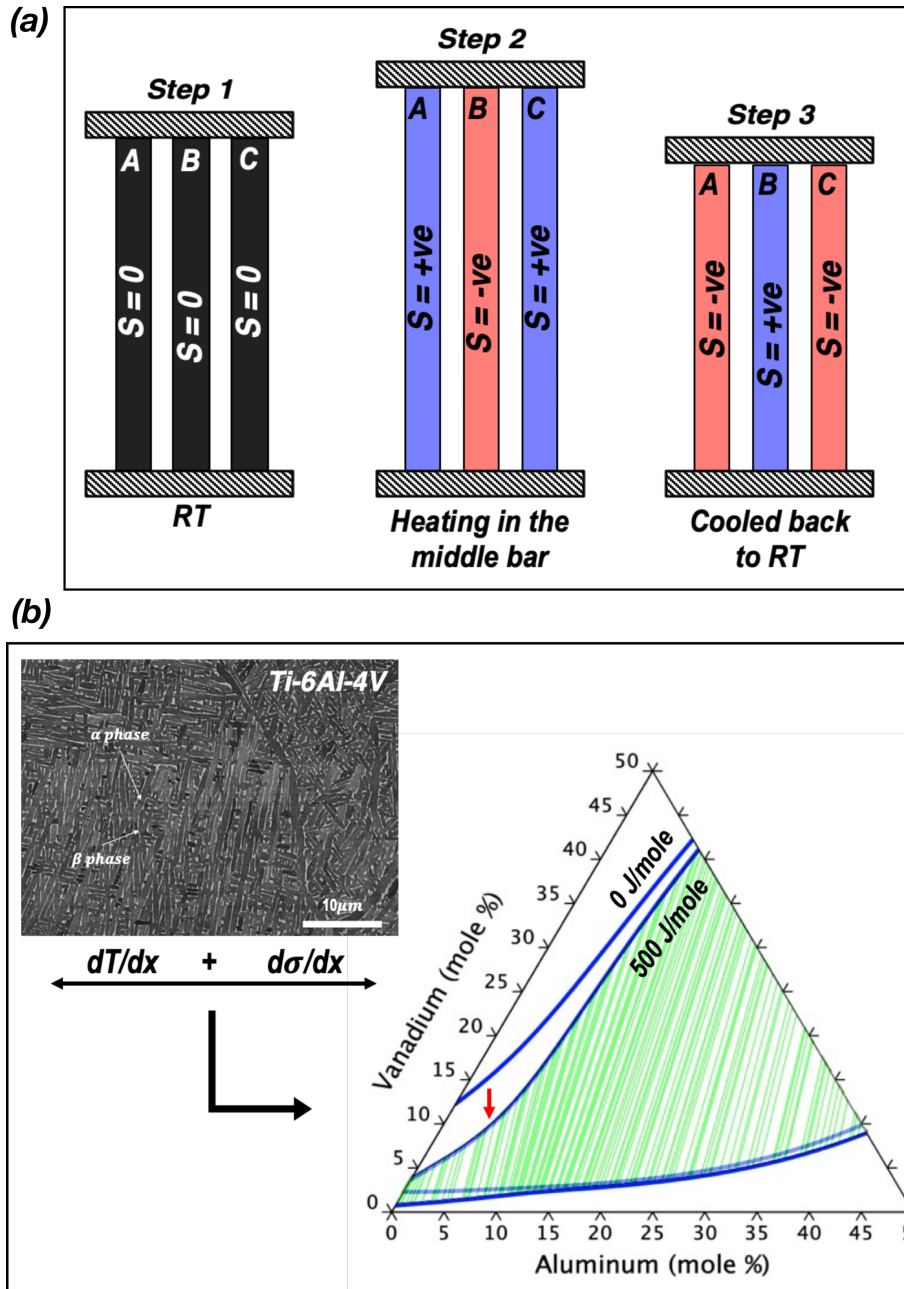


Figure 2.7: (a) Typical α/β microstructure in Ti6Al4V; (b) Schematic of Thermo-mechanical reversal experiments; (c) Evaluation with thermodynamic model.

this phenomena, as depicted in [Figure 2.7\(a\)](#). 3 vertical bars A, B and C are connected at both ends by a common rod with an initial stress state $S=0$. Bar B is now subject to a weld cycle. Depicted in Step 2, Bar B is heated and due to thermal expansion causing compressive stress in the bar. Due to the common rod connecting Bars A and C, tensile stresses are built in. During cooling to room temperature, bar B shrinks, pulling down the connecting rod (Step 3). As a result of the constraints given to the three rods by the common connecting rod, the influence of this shrinkage is felt in the surrounding bars A and C, where compressive stresses are now built-in, while tensile stress persists in bar B. And thus, in AM, due to the complex thermal cycles imposed in every voxel across a layer in an evolving geometry, it is possible for phases to be subject to non-uniform cyclic expansions and contractions within a constrained region.

We hypothesize that in AM of alloys, repeated thermal cycling with large fluctuating thermal gradients can lead to alternating localized compressive and tensile stress fields, dictated by the directionality of the thermal gradients. This might lead to complex plastic instability as well as microstructural modifications at the interfaces between phases. If the stress at any given region at a specific temperature is greater than the yield stress at that temperature, plastic strains preferential accumulate in either phase in the alloy [\[111\]](#). The impact of this preferential plastic strain partitioning between the α and β phases can have an effect on the inter-phase local thermodynamic equilibrium as depicted in [Figure 2.7\(b\)](#). Thermodynamic evaluation of the phase stability in Ti6Al4V, in the presence of added stored energy in the α phase is calculated using ThermoCalc[®], shows that an increased stored energy in the α phase (relative to the β phase) leads to a downward shift of the vanadium phase equilibria line (marked by the red arrow). Thus, it can be interpreted that in the presence of temperature and plastic strain gradients, the driving force for phase transformations is increased. With a variety of solid-solid phase transformation

pathways and a literature review on Ti6Al4V, we hypothesize that a reconstructive or displacive transformation is more likely to occur during dynamic phase transformations during complex thermo-mechanical reversals. Our goal is to analyze these transients with proper registration of macro thermo-mechanical signatures followed by an in-depth analysis on the strain partitioning behaviors and solute re-distribution between the α and β phases during dynamic transformations.

2.3.3 Tools used for capturing ex-situ and in-situ phenomenon

The objective of this study is to explore the phenomenological theories and the influence of complicated thermo-mechanical gyrations encountered during AM on a Ti6Al4V alloy. The Gleeble[®] thermo-mechanical simulator is the most effective tool for capturing the macro-scale flow behavior for our study. Characterization of the α/β microstructure post thermo-mechanical gyrations are analyzed with electron microscopy techniques (SEM, TEM and EBSD) to study the grain structure, texture, orientation and dislocation substructures in the alloy. With unique capabilities of Atom Probe Tomography, elemental partitioning across the α/β interface is examined to interpret the phase transformation pathway during thermo-mechanical reversals. In order to capture the temporal transients of plastic strains and dynamic phase transformations during thermo-mechanical reversals, in-situ experiments at the neutron (Vulcan Beamline, Spallation Neutron Source, ORNL) and synchrotron (FAST Beamline, CHESS) diffraction sources were employed. Using the benefits of high energy X-rays at the synchrotron beamlines, we were able to capture the spatial and temporal transient behavior of the solid-state phase transformation under fluctuating thermo-mechanical reversals.

CHAPTER 3

Ti6Al4V Cube builds and correlation with a Heat Transfer model

In this chapter, Ti6Al4V cube builds are fabricated via E-PBF with varying scan strategies. Each cube is then analyzed with respect to the spread of defects, microstructural features and textural variances of the α and β phases. A semi-analytical heat transfer model, also known as 3DThesis, developed at ORNL, is used to extract information on the spread of temperature fluctuations, thermal gradient and interface velocity across a layer for the scan strategies implemented in the build. The simulated signatures are then correlated with the microstructural features observed. By doing so, we are able to delineate the heterogeneities in an AM fabricated part subject complex thermal signatures during processing.

3.1 Analysis of Ti6Al4V cubes

3.1.1 *Cube fabrication and Scan strategies*

Cube shaped samples with dimension of 15 x 15 x 25 mm were fabricated via Electron Beam Powder Bed (E-PBF) on the ARCAM Q10+ machine at the Manufacturing Demonstration Facility (MDF), ORNL. The objective of this build is to evaluate the influence of varied

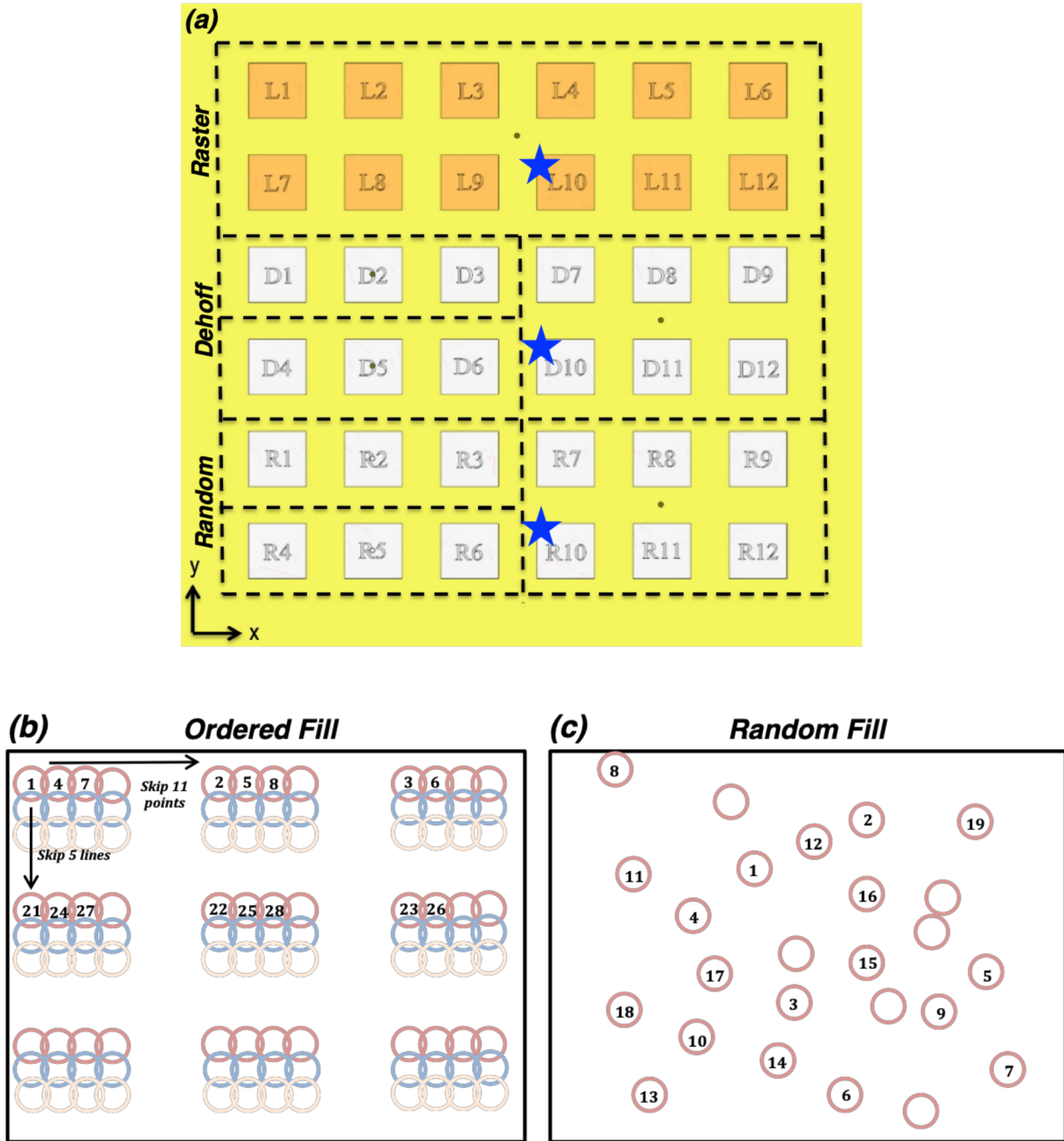


Figure 3.1: (a) Schematic of the fabrication of Ti6Al4V cubes on the baseplate where L, D and R stand for Raster scan, Ordered Spot fill and Random spot fill respectively; (b) Schematic of the Ordered Spot fill pattern; (c) Schematic of the Random Spot fill pattern.

energy inputs arising from the different thermal gyrations experienced across regions of the 3 cubes. The primary influence of the microstructure evolution within a geometry is the return time of the beam between neighboring points [116]. In order to achieve these variations, 3 different scan strategies are employed as shown in Figure 3.1. The Ti6Al4V cube builds are fabricated on a stainless steel base plate maintained at a pre-heat temperature of 475 °C. To avoid the influence of uneven input of beam current and speed during rastering, a turn angle of 67° about the z-axis, after every layer, is maintained. This further smooths out the volumetric energy input at a particular region. The next two scan strategies are spot melt scans (point source melting), where the cubes labelled ‘Rx’ are printed with a ‘random fill’ pattern and those labelled with ‘Dx’ are ‘ordered fill’. The ‘random fill’ scan pattern is one where individual spots are melted across the layer by a user-defined algorithm, such that each point on a layer has an equal probability of melting. The ‘ordered fill’ scan pattern is one where the layer is melted by spots such that every 11th point on a line is melted across the x-plane, followed by a gap of 5 lines in the y-plane, at which every 11th point would be melted and so on. The spot melt time for each spot was maintained at 0.3 ms.

To further have an effective distribution of the temperature across the builds, a grouping system is incorporated (marked by dashed black lines), where a group of 3 cubes is considered as one entity and likewise a group of 6 cubes. Therefore, the time taken to melt the second spot in the 6 cubes group will be twice as that of in the 3 cubes group. Each layer has a layer thickness of about 50µm. Thus, with these three melt scan strategies, variations in the evolving microstructure are expected due to the different excursions of thermal cycles each build experiences. As shown in Figure 3.1, 36 Ti6Al4V cubes were fabricated. The first two rows of cubes labelled ‘Lx’ is built using the raster (linear) scan pattern, and the rest of the cubes were built using a spot melt fill pattern (‘R’ for random and ‘D’ for Ordered spot fill).

From this entire set of cubes, our analysis will be focus on cubes ‘L10’, ‘D10’ and ‘R10’ from the group of 6 cubes.

3.1.2 *Porosity analysis on the cubes*

The ARCAM EBM system is equipped with an in-situ process validation tool, which is a high resolution near-infrared (NIR) camera (refer to ARCAM brochure for more details [34]). This NIR system captures images of each layer once melting has been completed before the raking of powders event occurs for the next layer. With variations in emissivity of IR radiations across hot spots, melted and unmelted regions across layers, defects such as porosities and irregular rake motions can be identified. Thus, with the in-situ capturing of each layer, combined with an image processing algorithm implemented as Dream3D filters, analysis of defects within the build is done [117]. It has been reported that for Ti6Al4V, the in-situ NIR monitoring can be effectively used in the detection of pores greater than 100 μ m in size [118].

A first look at the NIR images at a layer height of 12.7mm, where the intended ‘engineered defects were fabricated at the 4 corners of the builds, we notice that the pores were only visible in all the raster cubes and completely eliminated in both the spot melt cubes. The spatial and temporal transients of temperature for a spot melt is vastly different from that of a line melt [119]. In a line melt (raster scan), the melt pool is dragged along with the beam as the layer is being melted. Whereas, in the spot melt scan, individual melt puddles are formed as the layer is melted. Thus, the time taken to for the melt pool to solidify with respect to adjacent spots being simultaneously meted along with the underlying temperature of the previous layers, will vary. Thus, with a beam width of about 200 μ m, the resulting melt pool that was large enough to engulf the intended 500 μ m pores in the spot melt cubes. The limitation of the in-situ NIR monitoring system can be seen from the bottom 6 random

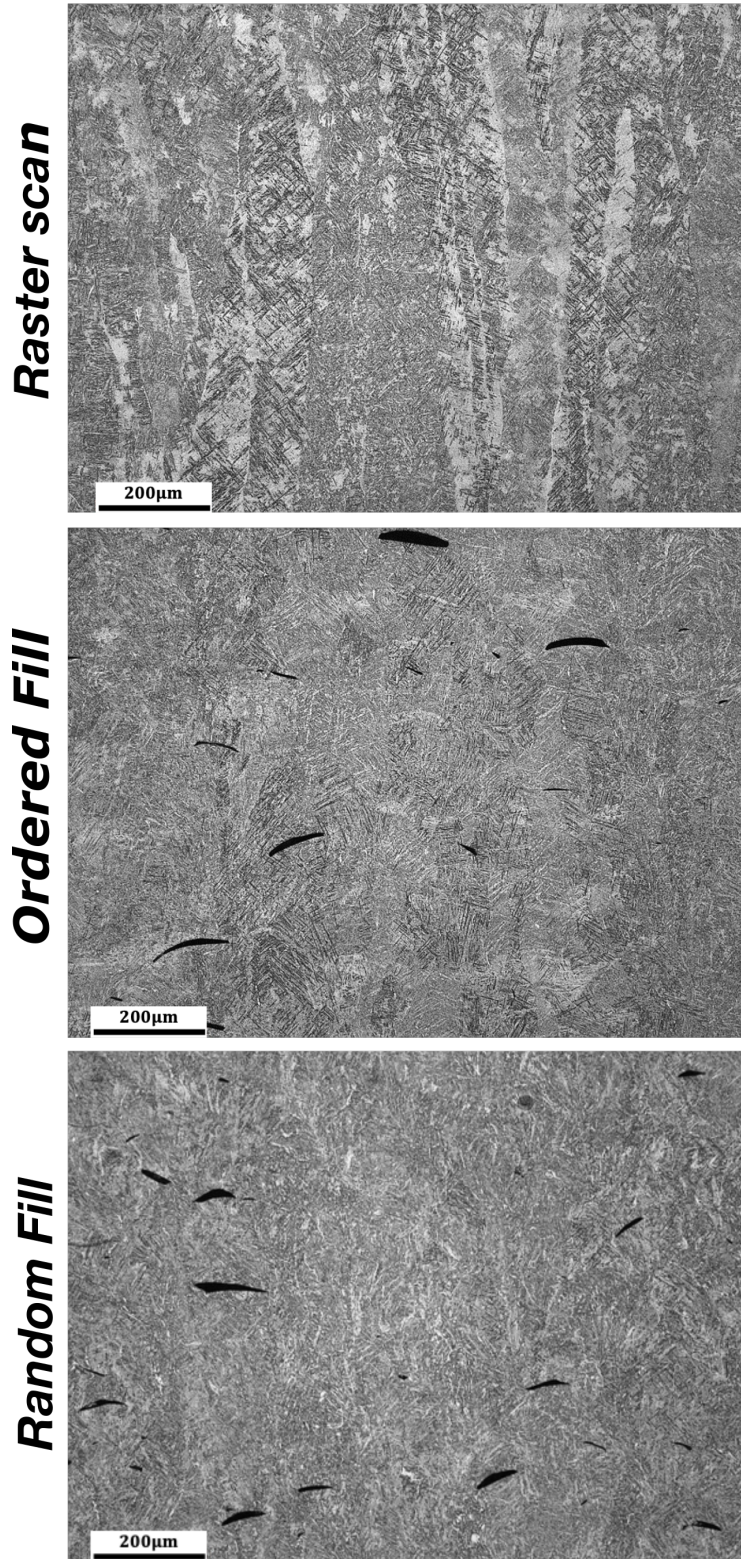


Figure 3.2: Optical images from the L10(linear), D10(ordered spot) and R10(random spot) cubes across the x-z plane. The spot fill patterns show more lack-of-fusion type defects when compared to the raster scan.

cubes. Since, NIR images are taken at the end of the melted layer, the last 6 cubes that were printed last are bright, since the temperature are still high in those cubes when compared to the other cubes.

A qualitative analysis of these defects is done with optical images across the x-y plane of the cubes and shown in [Figure 3.2](#). At a first glance, the increased porosity and defect in the spot scans is noticed. The crescent shaped defects seen in the D10 and R10 samples, resemble that of lack of fusion defects. Lack of fusion pores commonly arise at the intersection of weld pools within the same layer, due to the insufficient overlap of the weld pools. An insufficient weld pool depth, spot melt time and/or distribution of spots across the layer are all contributing factors to such defects [\[120\]](#). Since the spot melt scans from individual melt pools, it is possible that some regions may have cooled down faster before the adjacent region is being melted, thereby leaving behind an unmelted region. The impact of such pores has been studied before to have implications of the overall mechanical behavior of the part. In a recent study, McNeil et al. has shown the crack tendency is lessened/absent within a $\sim 100\mu\text{m}$ radius surrounding a large pore/defect [\[26\]](#). Thus, this raises the foundational question on the impact of macro-scale large and fluctuating thermal signatures on the sub-micron scale evolution of defect and pores and their impact on the local solid/solid interface kinetics and thermodynamics. Kenney et al. have shown the existence of a composition gradient on either side of a spherical pore, which resulted from the presence of a localized stress gradient surrounding the pore [\[121\]](#). The surrounding α and β microstructures did not deform, suggesting that the deformation of pores (local stress gradient surrounding the spherical pore) occurred before solid/solid transformation of β to the $\alpha+\beta$ microstructure.

3.1.3 *Microstructural characterization*

Analysis of the α and β microstructures across the 3 cubes (L10, R10 and D10) was done to evaluate the microstructural features and is shown in [Figure 3.3](#). SEM characterization was done on the Zeiss-Evo microscope with the back-scattered mode at 20kV. To enhance the microstructural features, samples were etched using Kroll's reagent. Images were taken along the x-z plane (along the build direction). All micrographs show a typical microstructure of α (darker grey regions) laths separated by thin β (white regions) ribs. The micrographs indicate a mixture of colony and basketweave or Widmanstätten α , which are all different morphologies of the α phase, within large prior- β grains. Quantitative analysis of these samples was done using ImageJ to analyze the width of the α lath. The width of the α laths across the 3 micrographs measured at an average value of 1.5 - 2.0 μm [[69](#), [122](#)].

The size of the α laths depend on the cooling rates from the β field (below β -transus temperatures) and is limited by the size of the prior- β grains [[65](#)]. Faster cooling rates ($\sim 410\text{K/s}$) render fine α laths, where slower cooling rates ($\sim 20\text{ K/s}$) allow for the growth/coarsening of the α laths [[15](#)]. The characteristics of the α laths play a important role in the strengthening of the alloy. For instance, finer α laths have shown to effectively reduce the slip length across the α laths, thereby improving the yield stress, ductility, crack nucleation resistance and crack propagation resistance (HCP strength) [[75](#)].

EBSD experiments were conducted across the top ($\sim 1\text{-}2\text{mm}$ from the topmost layer) and bottom ($\sim 1\text{-}2\text{mm}$ from the bottom layer) regions of the 3 cube samples to extract the α/β grain morphologies and textural variations. EBSD analysis was done on an Oxford System at a voltage of 5kV with a step size of 0.2 μm . Analysis of these EBSD maps were done with TSL-OIM software. Inverse Pole Figure (IPF) maps along the build direction (x-z plane)

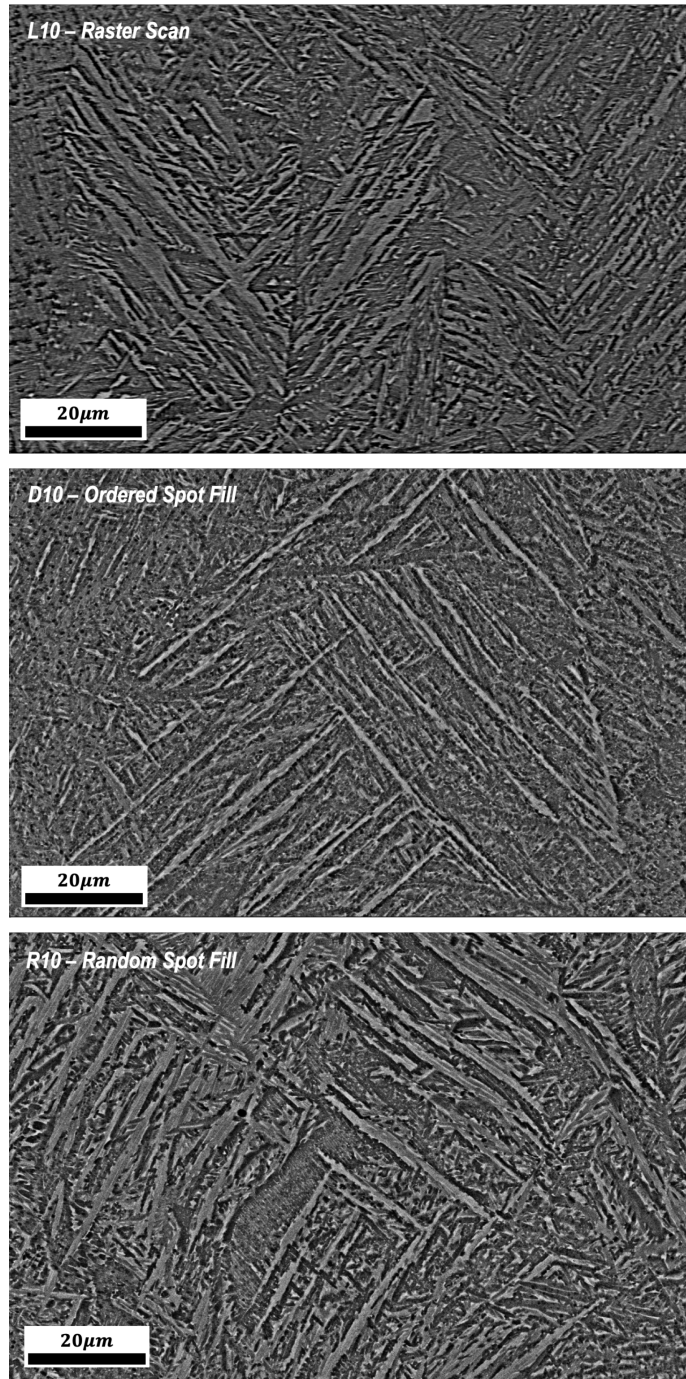


Figure 3.3: Back-scattered SEM micrographs of the L10(linear), D10(ordered spot) and R10(random spot) across the x-z plane highlighting α (darker grey regions) and β (white regions) morphology of the build.

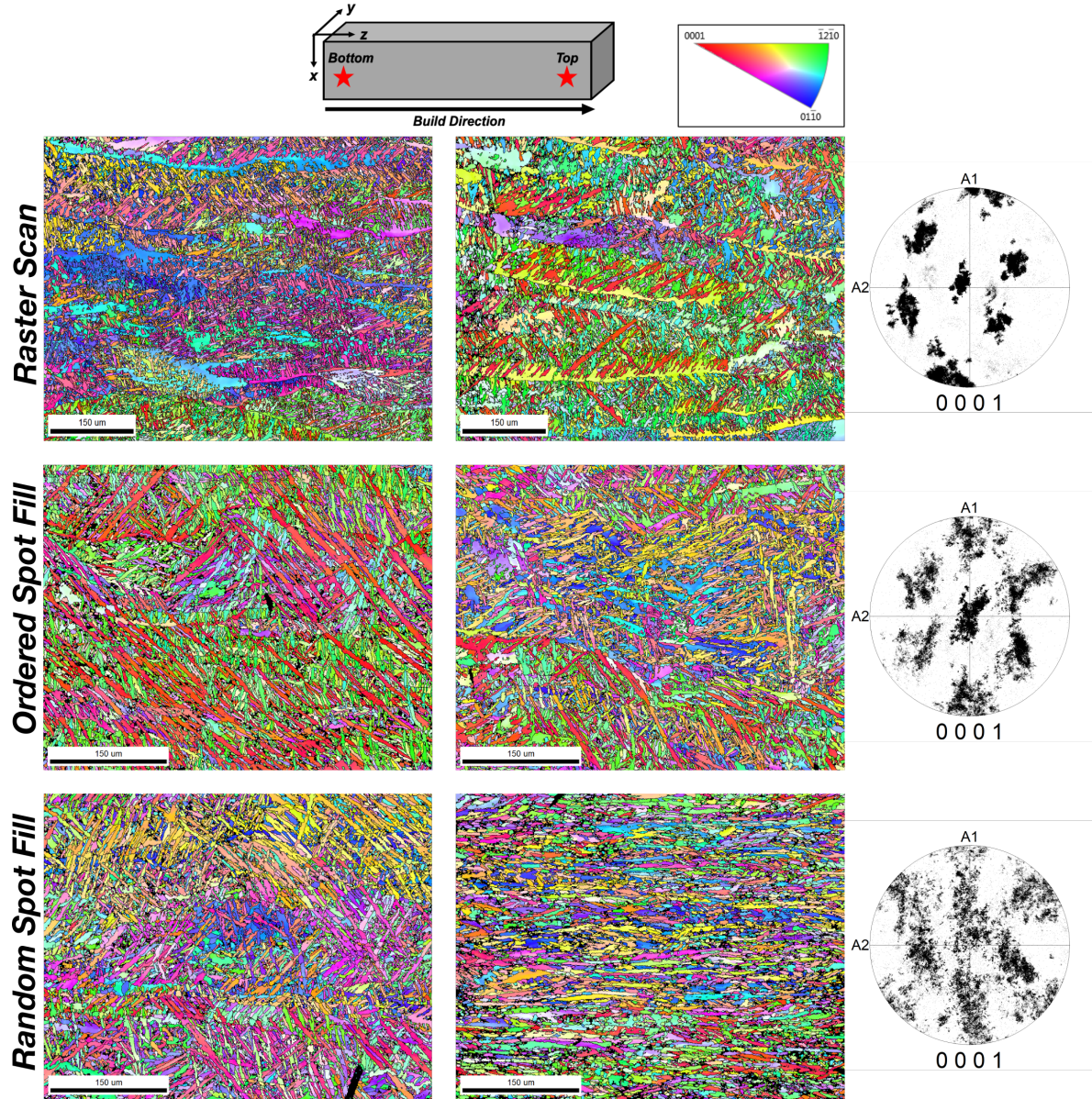


Figure 3.4: EBSD scans showing the IPF maps of the three cubes demonstrating variations in grain morphology from the bottom to the top of the build. Discrete pole figure of the (0001) basal plane, with the build direction along A2, of the IPF maps taken from the top of the build of the L10, D10 and R10 samples.

are shown in [Figure 3.4](#), revealing the α and β grain morphology at the bottom of the cube (left) and the top of the cube (right).

The raster cube shows a much finer microstructure than the spot melt cubes. The spot melt cubes, both random and ordered, show distinctively long α laths with high aspect ratios (10:1) at the bottom of the build. This observation can be rationalized on the number of thermal cycles experienced by each layer. Close to the bottom of the build, large thermal gradients exist due to temperature variations being high between the melting temperature of $\sim 1660^\circ\text{C}$ and the pre-heat temperature of 475°C . And so, sharper and faster cooling rates are experienced within the first few layers of the build [\[15\]](#). With increasing layers, the sharp thermal profiles are reduced due to the increased underlying temperature of the previously melted layers. The thermal gradients become shallower in the central regions of the build. Towards the top of the build, the long α laths are broken down into smaller α lath like structure, aligned along the build direction. This broken down α grain morphology can be explained by the temperature evolution, which will be discussed in detail in the following section. In short, towards the top of the build, the temperature is known to build up, thereby reducing the cooling rates. The random cube in specific shows the α laths, at the top of the build, all aligned along the build direction. Discrete pole figures are plotted to represent a graphical description of grain orientation with reference to a specific axis. The pole figure for the spot scans shows a slightly fiber type texture which can be seen from the above EBSD maps particularly seen from the random spot fill cube.

EBSD scans at higher magnifications were taken across the 3 builds (x-z plane, build direction marked by arrow) and Inverse Pole Figure (IPF) maps along with discrete pole figures of the $(110)\beta$ and $(0001)\alpha$, are shown in [Figure 3.5](#). The OIM analysis tool is used to determine the orientation relationships between phases in the region of interest. All the three cubes show a strong BO relationship $[(110)\beta \parallel (0001)\alpha]$ and the $[\bar{1}\bar{1}1]\beta \parallel [11\bar{2}0]\alpha$

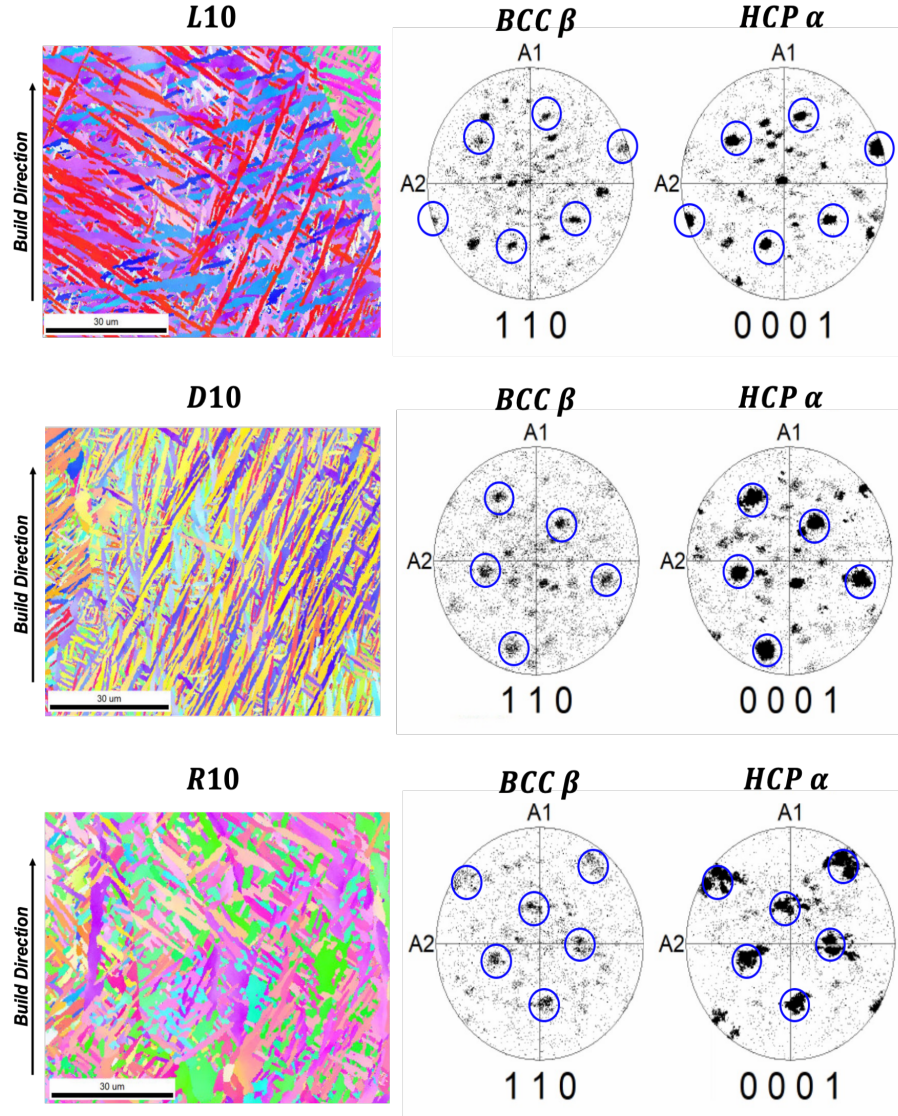


Figure 3.5: IPF maps and the discrete pole figure of the $(0001)\alpha$ basal plane and $(110)\beta$, with the build direction along A1, shown common poles indicating strong Burgers orientation relationship in the L10, D10 and R10 samples.

maintained between the β and α phase, marked by the blue circle pointing to common poles between the (110) β and the (0001) α . The intensity differences between the two pole figures can be accounted for due to the small β phase fraction. The average α/α inter-variant boundary misorientation analysis was done with the OIM analysis tool across the 3 samples for the IPF maps shown in Figure 3.5. The analysis revealed major peaks at positions of $\sim 10^\circ$, $58-60^\circ$ and $\sim 90^\circ$. Haghdadi et al. have shown that the low inter-variant misorientation boundary of 10.53° correspond to colony α microstructure, which can be seen from the IPF maps of the L10, D10 and R10 samples in our study [123]. The inter-variant misorientation around the 60° angle is most commonly seen in Ti alloys, more often demonstrating the ‘self-accommodating’ (reduction of the shear shape strain) theory of α variants in a triangular form [62, 93, 123, 124]. Although, texture analysis of the 3 cubes is not the focal point of this research, the above findings reveal that there is a degree of homogeneity in the microstructures that develop during AM processing. However, the physics underpinning the development of the many α variant clusters, $\alpha+\beta$ morphologies, and α lath thickness that emerge during AM in relation to spatial and temporal temperature transients has yet to be explored.

3.2 Semi-analytical Heat transfer model

3.2.1 Overview of the 3DThesis model

For many years, researchers have been working on building thermal, fluid, mechanical and thermo-mechanical models to describe the behavior of welds other deformation process [49, 112, 125–128]. In doing so, one can then optimize the appropriate process and parameters for a good build. To name a few in the scope of AM are the scan patterns, beam properties (E-beam or laser), material properties and the part geometry. Each of these variables has a large

impact in dictating the microstructure and properties of a build such as morphology of grains and texture, as well as macro-scale properties such as its mechanical behavior. It is known in AM that each layer experiences several thermal excursions through the liquid/solid and also solid/solid temperatures [13, 15, 16, 127]. Laser systems usually have higher temperature gradients because the background temperature is maintained at room temperature. Whereas in E-PBF systems, a pre-heat step is incorporated in order to reduce this thermal stress by reducing large temperature gradients. These temperature gradients and heat extraction rate dictate the interface growth velocity and in the combined form gives us information on the predominant morphology of the grain that will form.

One such model used in the this study is the Semi-Analytical Heat Transfer Model (SAHTM), also known as 3DThesis, developed here at the Manufacturing Demonstration Facility (MDF), ORNL [119, 129, 130]. The SAHTM model is used as a first approximation tool to predict the solidification parameters such as the thermal gradients, interface velocities and cooling rate in part and correlate them with the part microstructure in our study. The basis of the model is derived from the Rosenthal equation, which gives a three-dimensional steady state temperature field for a point source moving in the x-direction and is given by [119]:

$$T(x, R) = T_0 + \frac{q}{2\pi k} \left(\frac{1}{R} \right) \exp \left\{ -\frac{v}{2\alpha} (R + x) \right\}$$

Where T_0 is the initial temperature, q is the beam power, k is the thermal conductivity, α is the thermal diffusivity and R is distance between the point source and beam location. The transient model implemented in the SAHTM model is based on the work by Komanduri and Hou for arc and laser welding processes. Detailed description of the model can be found elsewhere [119]. In short, the model is based on a transient solution for a stationery circular ring heat source within a semi-infinite domain, constant and uniform material properties.

The model does not take into account the heat losses due to convection and vaporization. The transient behavior is achieved by integrating the above equation numerically, using Gaussian quadrature method, for the location of each point with a time dependent beam location. The integration time step is one variable that has to be considered as this parameter could either result in poor accuracy or unnecessary computation time as shown by Benjamin et al. [129].

3.2.2 *Tracking T, G and R with the model*

Using the 3DThesis model described above, simulations of the temperature distribution, thermal gradients and interface velocities across a layer is done. The input variables for the model cover the material parameters, beam parameters and simulation parameters. Material parameters include the pre-heat temperature of the build (475 °C as maintained during the build), critical temperature at which gradients are calculated, which is the solidus temperature of 990 °C and the liquidus temperature of 1600 °C, specific heat, thermal conductivity and density. The critical temperature described in the model here is the temperature at which thermal gradients are calculated. Thermal gradients are calculated on cooling below the critical temperature meaning that every time a point experiences a temperature drop from the critical temperature, the slope of that temperature change is taken as the thermal gradient. By doing so, we can simulate the gradient at the L/S and S/S transformation points. The beam parameters include the beam size, which was set as (200 x 200 x 1) μm , the absorption efficiency set to 80% and the beam power of 1200W. Area of simulation, resolution, time step and the mode of simulation are defined in the simulation parameters tab. Simulation were done across one layer with a 'z' depth, thus giving a volumetric spread of temperature, thermal gradients and interface velocities across the layer.

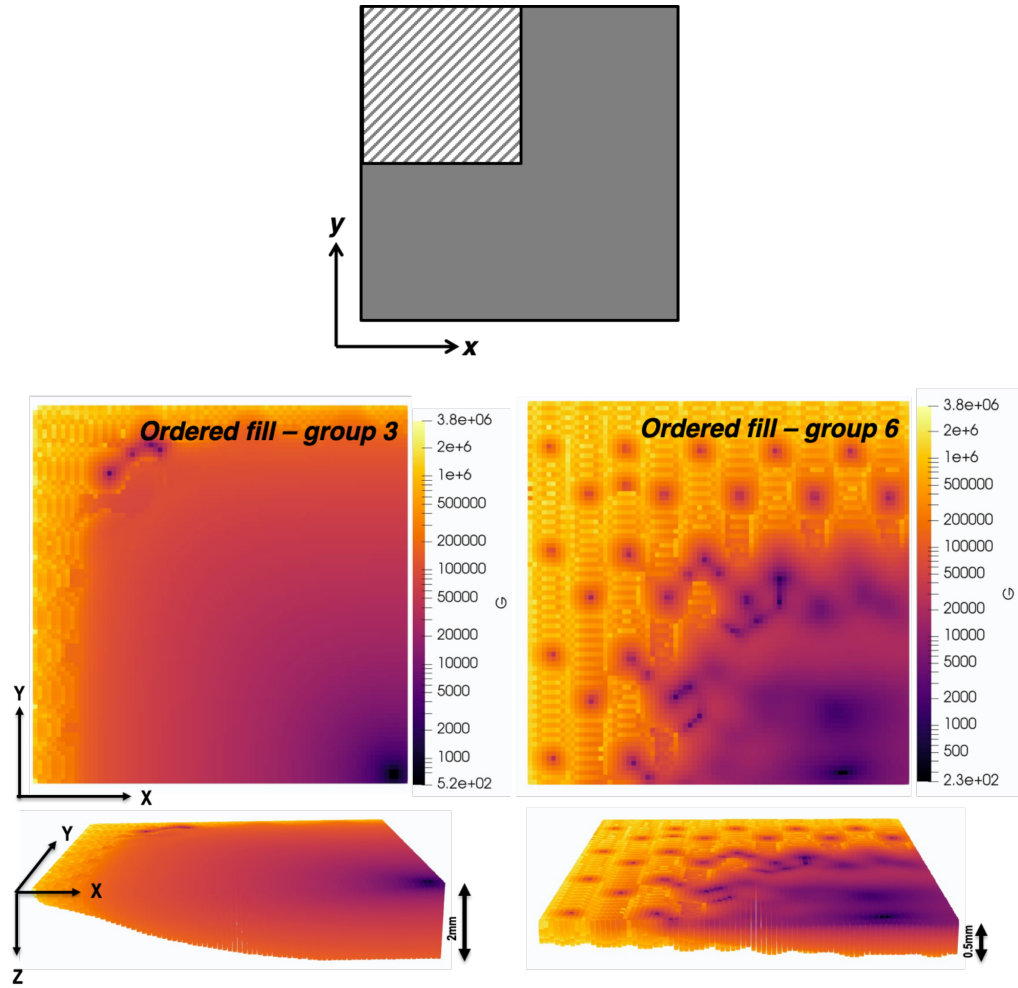


Figure 3.6: Differences in the spread of S/S thermal gradients as seen from the Ordered Spot Fill Scan grouping of 3 cubes (left) and the grouping of 6 cubes (right). Shaded area of the cube (top) indicated the area simulated.

Since the integration becomes more complex over time rendering it more time expensive and data heavy, only points around the melt pool are tracked with time, with the calculated points retaining its last value (Mode 2, defined in the simulation parameters tab). Furthermore, since the sample geometry is a cube, with the x-y plane being a squared area, only the top left quadrant of the cube was simulated to enhance simulation efficiency, as seen by the shaded region in [Figure 3.6](#). In our analysis, prime focus will be on the ordered spot fill and the random spot fill, emphasizing on the differences between the group of 6 and 3 cubes. Shown in [Figure 3.6](#) are the thermal gradient profiles (calculated at the solid/solid $\beta \rightarrow \alpha$ transformation temperature of 1000 °C), during the last time-step for which the heat source was active for the layer. The spot scans, as described above, are individual melt puddles that are melted in a user-defined sequence. Therefore, as more spots are being melted across the layer, the overall temperature at the center of the cube is much higher, forming a larger melt pool as the beam proceeds melting spots. This behavior is different from the raster scan, the melt pool is dragged along with the beam as it traverses from one end of the cube across to the other end, hence not concentrating the heat in the center of the cube. Comparing the effect of the return of spot time (grouping of the 3-cubes versus 6-cubes), the spread of the thermal gradient is much shallower than the grouping of 6 cubes. The impact of the S/S thermal fluctuations across a layer on the depth ('z' depth) below the current layer is shown in [Figure 3.6](#). It can be observed that the melting of the cube with the grouping of 3 affects approximately 2mm (*sim*40 layers) depth of material below it, whereas the melting of the cube with the grouping of 6 affects about 0.5mm (*sim*10 layer) depth of material below it. This demonstrated that changing the scan patterns caused changes in the distribution of temperature gradients and interface velocities in the part, which in turn dictated the phase transition route and microstructure characteristics.

Not only are the evolution of G and V important, but their combined form has more implication on the evolution of the solidification structure. From the distribution of the gradients and interface velocities, we can interpret what solidification microstructure is more likely to form, i.e., equiaxed, columnar or mixed [1, 29, 47]. The simulated values of thermal gradients and interface velocities across the Ordered Spot fill, Random spot fill and Linear Raster scan, fall in the columnar region of the predicted CET curve, shown in Figure 3.7. Columnar prior- β grains emerge as the primary solidification structure, and can be seen by the black dashed line marking prior-columnar β grains, followed by the decomposition of the $\beta \rightarrow \alpha + \beta$ on further cooling.

3.2.3 *Correlation of thermal gradients with microstructure*

The variations in the solid/solid thermal gradients, temperature changes and interface velocities for a location on a layer may be tracked, using the information from the above simulation results, as the layer is being melted. Shown below in Figure 3.8 is a plot of the evolution of the calculated thermal gradients from a random fill cube (group of 6), of a point at the center and a point at the corner of the cube. A stark difference in the thermal gradient fluctuation can be noticed from the two points. A point at the corner of the cube, experiences large thermal-gradient (2×10^6 K/m) with a lower frequency of thermal fluctuations, since the surrounding regions are powder particles and so individual melt pools are cooled rather drastically. In addition, a lower frequency of fluctuations is noticed, and this is because a point at the corner has fewer adjacent points. Whereas the point at the center of the cube experiences shallower thermal gradients (4×10^4 K/m), because as the surrounding points get melted, a large melt area is created at the center of the cube, but with a higher frequency of fluctuations. It is noteworthy to mention that the above fluctuations are tracked across a single layer, with a preheat temperature of 475°C . As additional layers are added on, these

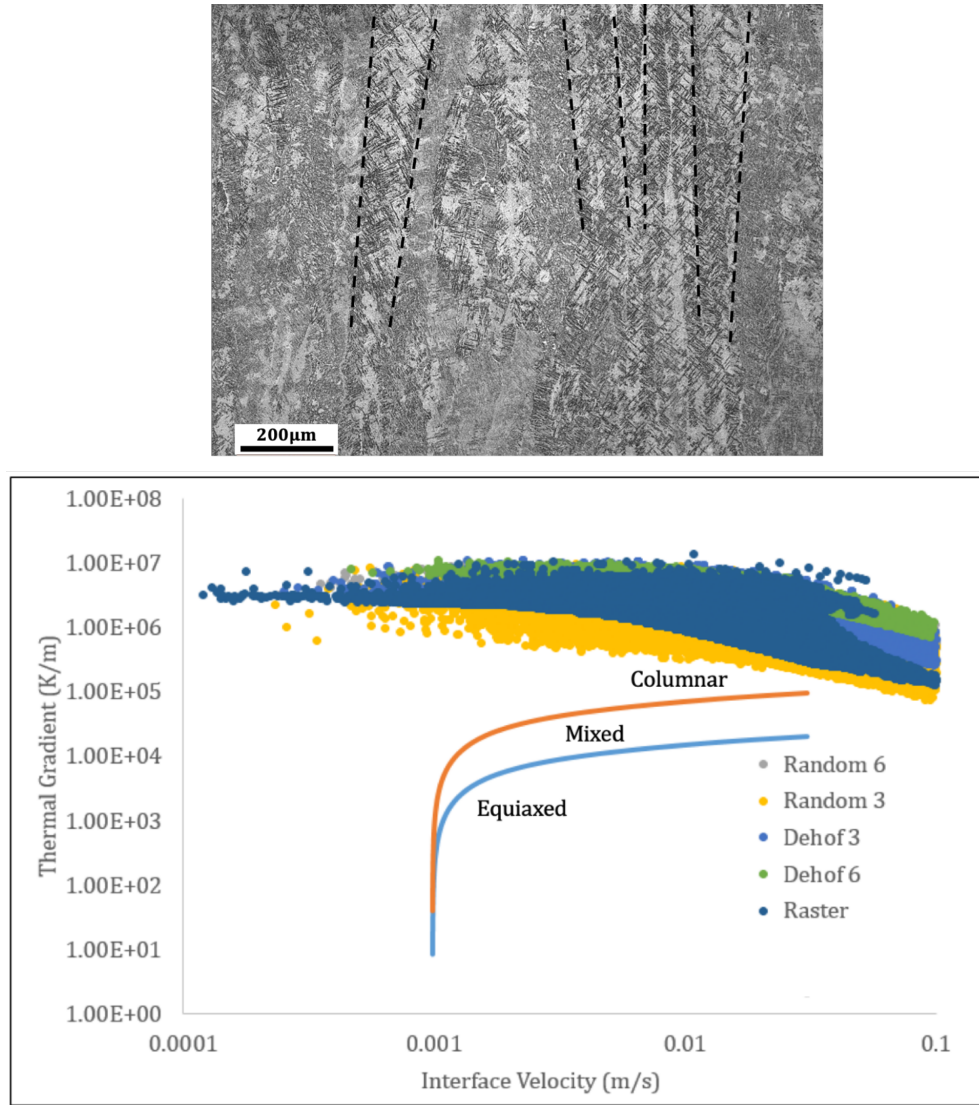


Figure 3.7: SEM image of the raster scan pattern where the prior beta grain are marked by black dashed lines. Shown below is the CET curve for Ti6Al4V and the simulated spread of GV showing all the build are in the columnar region.

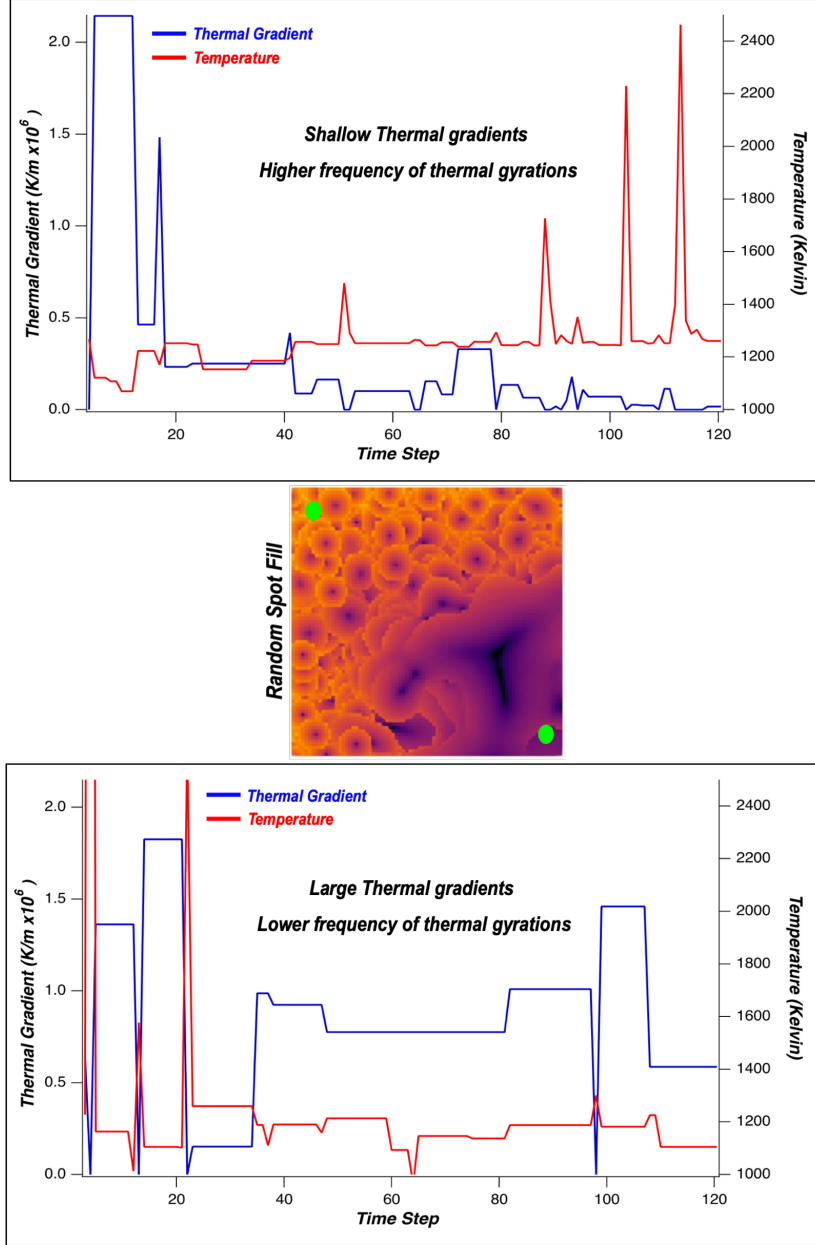


Figure 3.8: Tracking the evolution of the thermal gyrations for a point from the center and corner of the cube.

fluctuations increase and from our previous result, we know that the impact of melting of a single layer in the group 6 cubes influences a z-depth of $0.5\mu\text{m}$ below the current layer (about 10 layers). Thus, the fluctuations a region/point undergoes is amplified as the number of layers increases.

By being able to track these fluctuations, a correlation can be done to the microstructure at these specific locations and is shown in [Figure 3.9](#). Regions at the center of the cube have longer α laths separated by thicker β ribs, and a more basket-weave morphology. This morphology of α occurs on slower cooling rates ($\sim 1 \times 10^4$ K/s calculated from the above G and R predicted values), which relates back to the shallower thermal gradients at that center of the cube. At the corner of the cube, where thermal gradients are higher with faster cooling rates ($\sim 9 \times 10^4$ K/s) the α morphology is more broken down and shorter with much narrower prior β grains. This indeed shows the impact fluctuating thermal gradients can have on the resultant $\alpha + \beta$ morphology.

3.3 Summary of chapter

This chapter can be summarized as:

(1) Ti6Al4V cube samples were fabricated with a (1) bi-directional raster scan and two spot melt scans, a (2) random spot fill and a (3) ordered spot fill. The 3 different scan strategies was designed to impose variations of the temperatures and thermal gradients across the build. The impact of the variations of thermal fluctuations can be noticed in the microstructural evolution of the α and β phases across the build direction of the build. The builds fabricated with the spot fill scans showed a larger concentration of porosity's and lack of fusion defects when compared to the raster scan cubes.

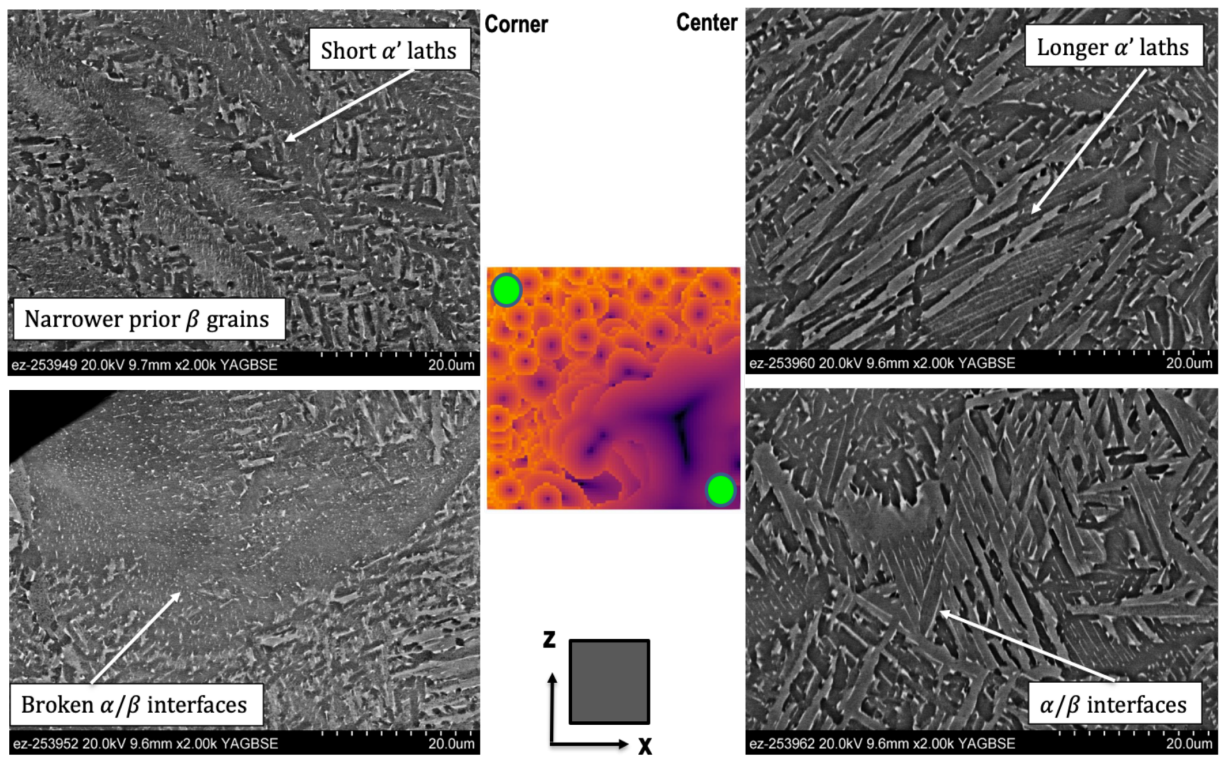


Figure 3.9: Microstructural variation from a point in the center and corner of the cube.

(2) Irrespective of the scan strategy, strong Burger’s orientation relationships is maintained between the α and β phase with the significant inter-variant misorientation angles at $\sim 10^\circ$, $\sim 58\text{-}62^\circ$ and $\sim 90^\circ$. These findings correspond well with published literature of inter-variant boundaries studied on similar Ti6Al4V builds [53, 123, 131].

(3) A semi-analytical heat transfer model is used to interpret the distribution of temperatures (T), thermal gradients (G) and interface velocities (R) across a layer in the build. The 3DThesis model projected columnar grains as the primary solidification morphology on cooling based on the simulated values of G and R. This can be seen from the ex-situ characterization via SEM and EBSD analysis revealing long columnar prior β grains [54, 132].

(4) The investigation of the α and β microstructural gradients across the Ti6Al4V build fabricated with 3 scan methods reveals that unexplained heterogeneity in the solid/solid phase transformation kinetics, still persist during AM processing. For instance, similar ex-situ characterization analysis on the Ti6Al4V indicated that although, strong BO relationship is maintained between the parent β and α grains, the spread of inter-variant boundaries (more commonly the $60^\circ[11\bar{2}0]$ in colony and basket-weave type α and $63.26^\circ[10\bar{5}5\bar{3}]$ in acicular α) vary across the 3 cubes [53, 123, 131]. Meanwhile Quintana et al. and Shao et al. analysis on the Ti6Al4V cubes (spot fill cubes from the group of 3), show variations of texture, α lath thickness and size of the prior- β grain along the length of the cube across the length of the cube [54, 69]. The above-mentioned studies show that columnar prior- β grains grow along the (001) easy growth direction (the build direction). Nonetheless, due to the spatial and temporal transients of temperature fluctuations as layers are melted, the resulting $\alpha+\beta$ microstructure vary across the builds.

(5) Aside from microstructural gradients across the build, there has been a long-standing discussion about the $\beta \leftrightarrow \alpha'+\beta \leftrightarrow \alpha+\beta$ transformation kinetics as successive

layers are melted. Due to fast cooling rates, martensitic α' is the primary product from the high temperature BCC β phase on cooling and on subsequent thermal cycles, this then decomposes to $\alpha+\beta$. Nevertheless, questions revolve around α phase in terms of variant selection and on the stability of the β phase on subsequent cycles. These uncertainties have not been addressed in relation to the development of local plastic instabilities in an evolving component as a result of fluctuating temperature gradients, and thus leads us to explore these transients in the following chapters.

CHAPTER 4

Thermo-mechanical reversals and In-situ Neutron Diffraction study

The observations made from the preceding chapter led us to address the $\alpha \leftrightarrow \beta$ phase kinetics in Ti6Al4V during thermo-mechanical reversals. The pathway we chose to address these transients is by studying the impact of thermo-mechanical (TM) gyrations on the strain partitioning between the α and β phases in Ti6Al4V. Thermo-mechanical reversals were imposed on an AM E-PBF Ti6Al4V sample on a Gleeble[®] thermo-mechanical simulator. Following the observations from the rapid TM experiments, in-situ experiments were conducted at the Vulcan Beamline, Spallation Neutron Source, Oak Ridge National Laboratory, to resolve the temporal transients of the events. Results from these TM experiments are interpreted with Neutron Diffraction, SEM and EBSD analysis. The details entailed in the chapter has been published in Materialia journal [133].

4.1 Experimental setup

4.1.1 *Thermo-mechanical simulator*

Gleeble[®] Thermo-mechanical simulator and experimental setup:

Thermo-mechanical cycles were carried out on the Gleeble[®]3500 thermo-mechanical simulator as shown in [Figure 4.1](#). The Gleeble is an equipment used for dynamic thermal and mechanical testing of materials, thereby enabling the physical simulations of processes. As the focus of our experiments is on the impact of rapid thermo-mechanical fluctuations experienced during AM, the Gleeble[®] was the ideal choice of equipment. K-type thermocouples were attached to the sample to track the temperature readings throughout the experiment.

Framework of Thermo-mechanical reversals:

Out-of-phase constant-strain thermo-mechanical reversals were conducted on all our samples. Strain amplitudes of 0.8%, 1.0% and 1.2% were chosen with temperature ranging between a lower temperature limit of 400 °C to the upper temperature limits of 650 °C and 700 °C. This particular temperature range was chosen to study the phase kinetics in the solid-solid transformation regime in Ti6Al4V under fluctuating thermo-mechanical reversals. Strain limits were chosen in order to impose plastic strains into the material during fluctuations. Thermal rates were chosen to replicate the fast heating and slow cooling rates experiences during AM melt cycles and so, a heating rate of 50 °C/s and a cooling rate of 10 °C/s was chosen. Thus one thermo-mechanical cycle, as shown in [Figure 4.2](#), occurs by the ramp up of temperature from 400 °C to 650 °C as a simultaneous compressive strain of 0.01mm/mm is applied. The sample is then held for 5 seconds and then on cooling back to 400 °C, a tensile strain of 0.01mm/mm was applied. Since EBM has the unique capability of maintaining a

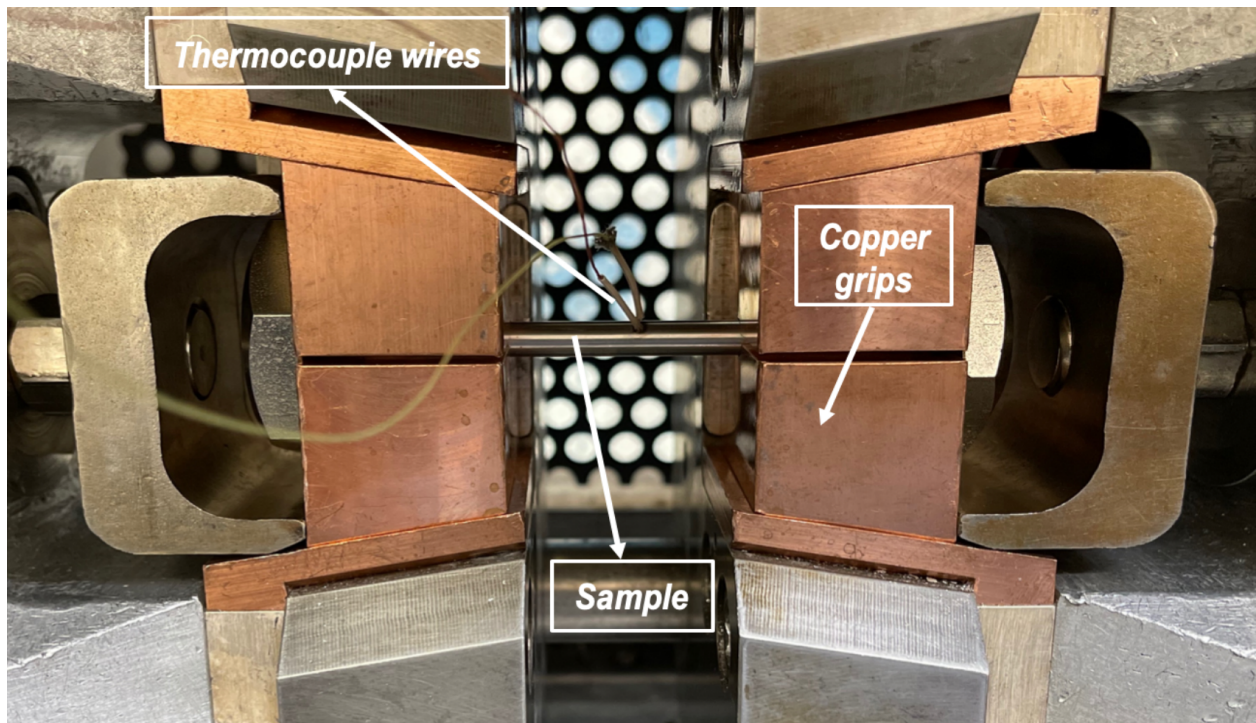


Figure 4.1: Ti6Al4V sample loaded in a Gleeble[®] 3500, with attached thermocouples to monitor temperature.

pre-heat temperature throughout the build, which in Ti6Al4V ranges from 400 °C to 660 °C, the lower temperature was set at 400 °C for all experiments. The upper temperature range was chosen from a literature survey, where in one study done by Elmer et al., a noticeable change in the lattice parameter of the β phase occurs in this temperature range [134].

Sample fabrication:

Cylindrical Ti-6Al-4V samples were fabricated using the E-PBF process, on the ARCAM system with a pre-heat temperature of 475 °C maintained throughout the build. A block of Ti-6Al-4V was built using a raster pattern, from which individual cylindrical samples, 6mm in diameter and 110mm in length, were EDM cut to the required dimensions. An AM sample is specifically chosen for our experiments so that the underlying material property resembles that of an AM build, so as to fully grasp the impact of the thermo-mechanical reversals.

4.1.2 Neutron Diffraction Setup and Characterization Tools

Neutron Diffraction:

Neutron Diffraction experiments were conducted at the VULCAN beamline at the Spallation Neutron Source (SNS), ORNL [135]. There are two detector banks ($2\theta = \pm 90^\circ$) that simultaneously collect diffracted neutrons. Bank 1 collects diffracted neutrons from the planes whose normal are along the axial (loading direction) and Bank 2, from planes whose normals are along the transverse direction of the sample, as shown in Figure 4.3. Since neutrons have a high penetration depth and hence give a more bulk analysis, this technique was chosen for our study. A neutron gauge volume, defined by the slit sizes and receiving collimator, was maintained at (8 x 6 x 5) mm with a nominal flux (60Hz) of $6.7e7$ n/s/cm².

Time-of-flight diffraction data is used to measure the specific (hkl) lattice strains in the α and β phase, given by the following equation (Equation 4.1).

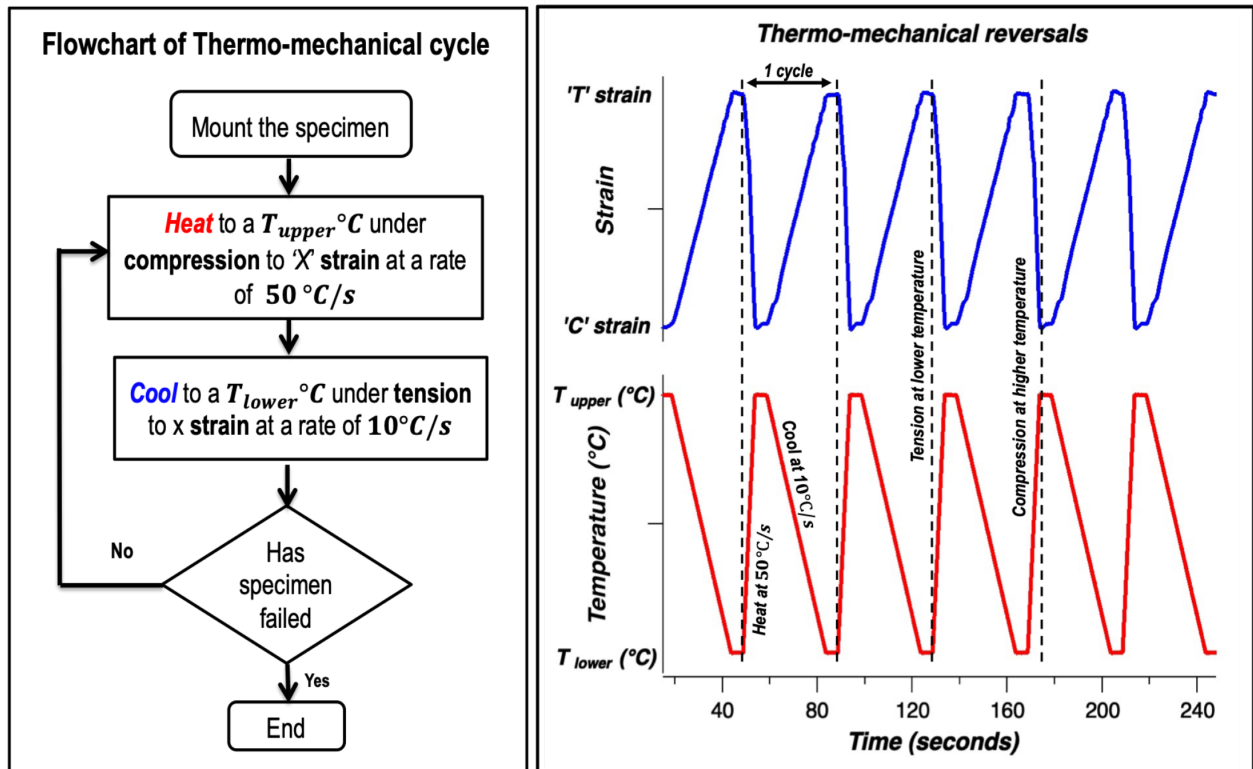


Figure 4.2: (Left) Flowchart of the thermo-mechanical test; (Right) Schematic of the simultaneous temperature and strain reversals highlighting the out-of-phase thermo-mechanical reversals.

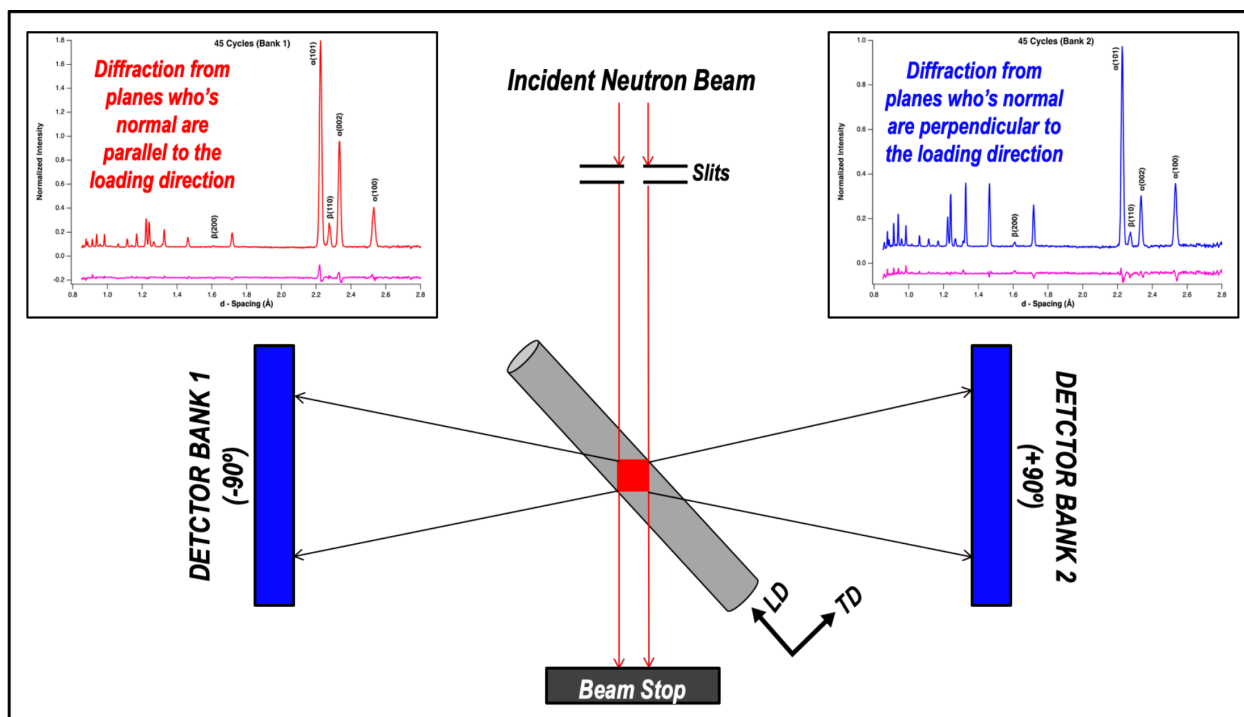


Figure 4.3: Detector and Sample orientation at the VULCAN beamline, SNS.

$$\epsilon_{(hkl)} = \frac{d_{(hkl)} - d_{o(hkl)}}{d_{o(hkl)}} \quad (4.1)$$

$\epsilon_{(hkl)}$ is the lattice strain in the $\{hkl\}$ plane, $d_{(hkl)}$ is the interplanar spacing of the strained $\{hkl\}$ plane under loading and $d_{o(hkl)}$ is the initial interplanar spacing of the sample before cycling (measured at room temperature). Single peak fitting of the individual $\{hkl\}$ peaks [$\alpha(100)$, $\alpha(002)$, $\alpha(101)$, $\beta(110)$] was done using the VDRIVE software [135, 136]. Time-of-flight versus Intensity data was refined and analyzed using the EXP-GUI program. The lattice parameter and the phase fraction of each phase were extracted as the result of Rietveld refinement. In order to compensate for the inherent texture in the AM samples, the spherical harmonic preferred orientation option was selected during refinement, for both the α and β phases. Details on this texture model can be found elsewhere [137].

Microstructure Characterization:

Metallographic analysis of the samples was done using a JEOL 6500 SEM to examine the α and β microstructures. Samples were polished down to a colloidal silica finish and etched with Kroll's reagent (100 ml water + 6ml Nitric acid + 3ml Hydrofluoric acid) to distinguish the α and the β phases. Selected regions of interest from the gage section (sectioned parallel to the loading direction) were analyzed. SEM images were taken across various regions of the gauge section to ascertain the characteristics of the two phases. Electron Back Scattered Diffraction (EBSD) was done in order to understand the grain structure and orientation features of the individual phases. A voltage of 20kV and a step size of 0.2 μ m was used for all EBSD maps.

4.2 Baseline Rapid Thermo-mechanical Reversals

4.2.1 *TM reversals between 400°C and 650/700°C*

Thermo-Mechanical fatigue of any metal may lead to softening or hardening depending on the underlying material behavior [138]. As briefed in the earlier section, our thermo-mechanical cycles were set to be out-of-phase, where compression was applied on heating, and tension on cooling. This methodology has shown to be ideal in maintaining the total strain reversals without buckling and barreling of the sample.

TM reversals between 400°C and 650/700°C:

The common factor from all the thermo-mechanical tests is the gradual reduction in stress as repeated thermo-mechanical cycles are imposed, i.e., an asymmetric softening behavior, shown in Figure 4.4. The results from the thermo-mechanical experiments are plotted as hysteresis stress-strain curves shown in Figure 4.5, where it can be seen that the reduction of stress on compressive side is more pronounced than that on the tensile side. In addition to this, an increasing trend in the stored energy of the system with increasing strain is noticed. Interestingly, as the strain amplitudes are increased, the stresses required to strain the alloy increases, since material properties are temperature dependent. For instance at 650 °C, the stress required to achieve a compressive strain of $\epsilon=0.008$ is -350MPa, whereas in order to achieve a compressive strain of $\epsilon=0.012$, the stress required to strain the sample was -430MPa. Observing the shapes of the Hysteresis curves, one can clearly note that the higher strain amplitudes resulted in larger plastic strain accumulation. The sample is then cooled to 400°C, and a tensile strain was applied to reset the compressive strain to zero and move on to a tensile strain. At this point, the tensile stress required to strain the material is around +600 MPa. These temperature and strain reversals are repeated up to a total of

75 cycles. One of the important findings from this result is an increase in the softening rate (i.e. stress relaxation rate) on arriving at 400 °C. For instance, looking closer at the 400 °C - 650 °C / $\epsilon = 0.010$ strain sample, the tensile stress on arriving at 400 °C in the first cycle was at 639 MPa and as the end of the 5-sec iso-thermal hold the stress measured to be 620 MPa. Interestingly, after 75 thermo-mechanical gyrations, the stress reduced from 596 MPa to 486 MPa within the same time frame of 5 seconds. This result confirmed our hypothesis that the cyclic thermal gyrations will indeed lead to different constitutive response in the Ti6Al4V alloy.

4.2.2 *Phase fraction analysis of the rapid TM experiments*

Phase fraction analysis of the α and β phases of the samples subject to rapid thermo-mechanical reversals between 400 °C and 700 °C were measured via neutron diffraction and tabulated in [Table 4.1](#). Each sample was placed in the path of the neutrons and measurements were integrated over a 1-hour exposure time. The resulting peak intensity versus d-spacing data are plotted for Bank 1 and Bank 2 individually and are shown in [Figure 4.6](#).

In order to have a state of reference for comparison, one of the samples subject to no cycling (marked as uncycled on the graph) is analyzed. Analysis from our reference state shows an initial reading of the α phase fraction of $97.31 \pm 0.2\%$ and the β phase fraction of $2.69 \pm 0.2\%$ from Bank 1 and an initial α phase fraction of $98.35 \pm 0.3\%$ and a β phase fraction of $1.65 \pm 0.3\%$ from Bank 2. Interestingly, in all the thermo-mechanically cycled samples, the $\beta(110)$ peak is now a separate distinct peak, appearing at around $d=2.28 \text{ \AA}$. Analysis on these samples revealed an increase in the β phase fraction in all the samples subject to thermo-mechanical reversals, where the β phase fraction increased from an initial of around $2.69 \pm 0.2\%$ to $\sim 5\%$. Thus, it is inferred that rapid thermo-mechanical reversals led to a dynamic $\alpha \rightarrow \beta$ transformation leading to a more stable β phase. A shift in the lattice

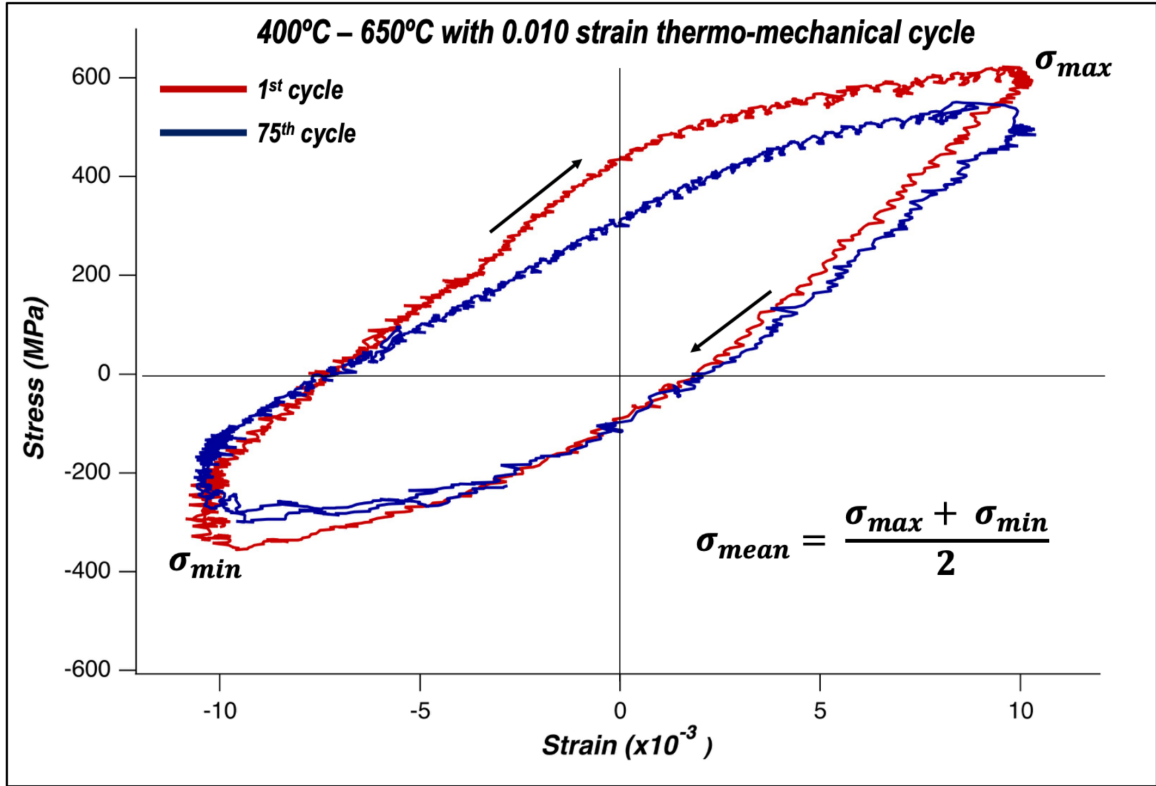


Figure 4.4: A closer look at the softening behavior from the hysteresis stress-strain curve, as shown from the 1st and last cycle (400 °C-650 °C + 0.010 strain amplitude); Mean stress is calculated by as the algebraic mean of the maximum and minimum stress in the cycle.

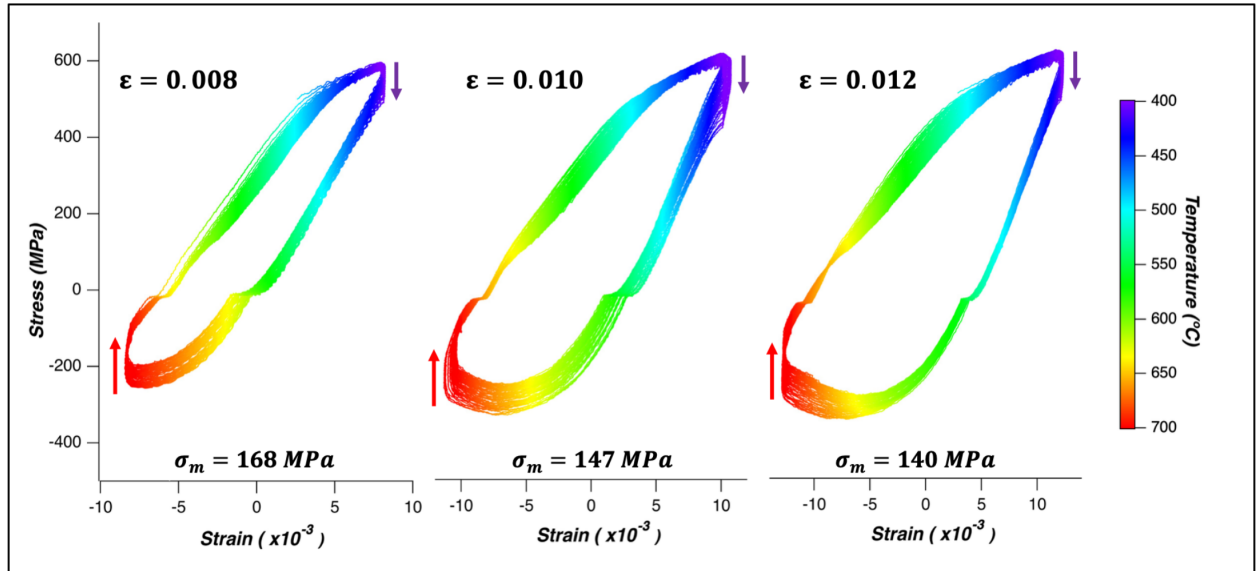
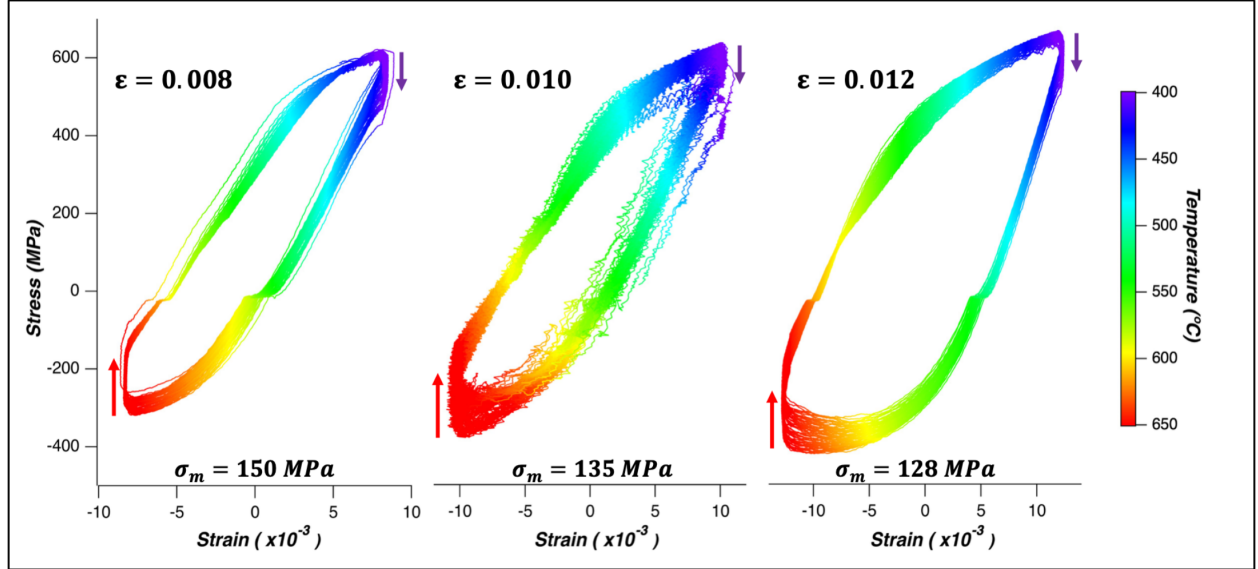


Figure 4.5: Hysteresis stress-strain curves as result of the out-of-phase thermo-mechanical reversals at strain amplitudes of 0.8%, 1.0% and 1.2% between temperatures of 400 °C and 650 °C(top)/700 °C(bottom). The mean stress of the last cycle in each TM reversal is noted below.

<i>Detector Bank</i>	<i>Bank 1</i>		<i>Bank 2</i>	
<i>TM_cycle/Phase</i>	α (wt.%)	β (wt.%)	α (wt.%)	β (wt.%)
<i>400°C-650°C</i> <i>0.008</i>	95.21 $\pm$ 0.02	4.78 $\pm$ 0.03	94.78 $\pm$ 0.02	5.22 $\pm$ 0.03
<i>400°C-650°C</i> <i>0.010</i>	94.89 $\pm$ 0.02	5.51 $\pm$ 0.03	95.31 $\pm$ 0.02	4.72 $\pm$ 0.02
<i>400°C-650°C</i> <i>0.012</i>	95.34 $\pm$ 0.02	4.65 $\pm$ 0.02	95.99 $\pm$ 0.02	4.98 $\pm$ 0.03
<i>400°C-700°C</i> <i>0.008</i>	93.73 $\pm$ 0.03	6.26 $\pm$ 0.03	95.02 $\pm$ 0.02	4.95 $\pm$ 0.02
<i>400°C-700°C</i> <i>0.010</i>	94.05 $\pm$ 0.02	5.94 $\pm$ 0.02	94.97 $\pm$ 0.02	5.00 $\pm$ 0.02
<i>400°C-700°C</i> <i>0.012</i>	94.47 $\pm$ 0.02	5.52 $\pm$ 0.03	95.38 $\pm$ 0.02	4.62 $\pm$ 0.03

Table 4.1: Measured α and β phase fraction and lattice parameters across the thermo-mechanically cycled samples.

parameter of the β phase from $a_0=3.21 \pm 0.0002 \text{ \AA}$ to $a_0=3.23 \pm 0.0001 \text{ \AA}$ was noticed. At this juncture, it is noteworthy to mention that an increase in the β phase fraction, when subject to a uni-axial tensile loads, has been previously reported in literature for $\alpha+\beta$ titanium alloys [86].

4.2.3 *Microstructural Characterization*

A detailed scanning electron microscopy analysis of the gauge section was performed. Two distinct types of microstructures were noticed, a broken-up α/β microstructure and a distorted α lamella, Figure 4.7. The region of the break-up α lamella consists of small and broken down β ribs separating the α into smaller regions. Accumulating strains due to the thermo-mechanical cycles, provide a driving force for the β phase to grow into the α phase, causing it to break up. The distorted α lamella is a morphology that developed within the α lamella due to variations in the local stresses during deformation [139].

EBSD analysis was performed on the gauge section and the motivation for this additional analysis was to further understand the phase transformation kinetics during TM reversals. The sharp $\beta(110)$ peak seen in Figure 4.6 can be a consequence of two phenomena: (i) an increase in the β phase fraction in the presence of localized strain gradients due to new β grain nucleating with a different orientations; or (ii) a change in the texture of the β grains that occurs when subject to thermo-mechanical reversals. Since the neutron data is collected from just two detectors at 90° to each other, the entirety of the texture behavior cannot be de-convoluted. EBSD patterns were taken along the loading direction (build direction) (XZ plane) at the sample gauge section. The EBSD results comprising of inverse pole figure maps, grain misorientation maps and phase maps are shown in Figure 4.8. All the regions in green, in the phase map correspond to the BCC β phase, whereas those in red to the α phase. Regions of high mis-orientation are seen at the boundaries of the α phase and

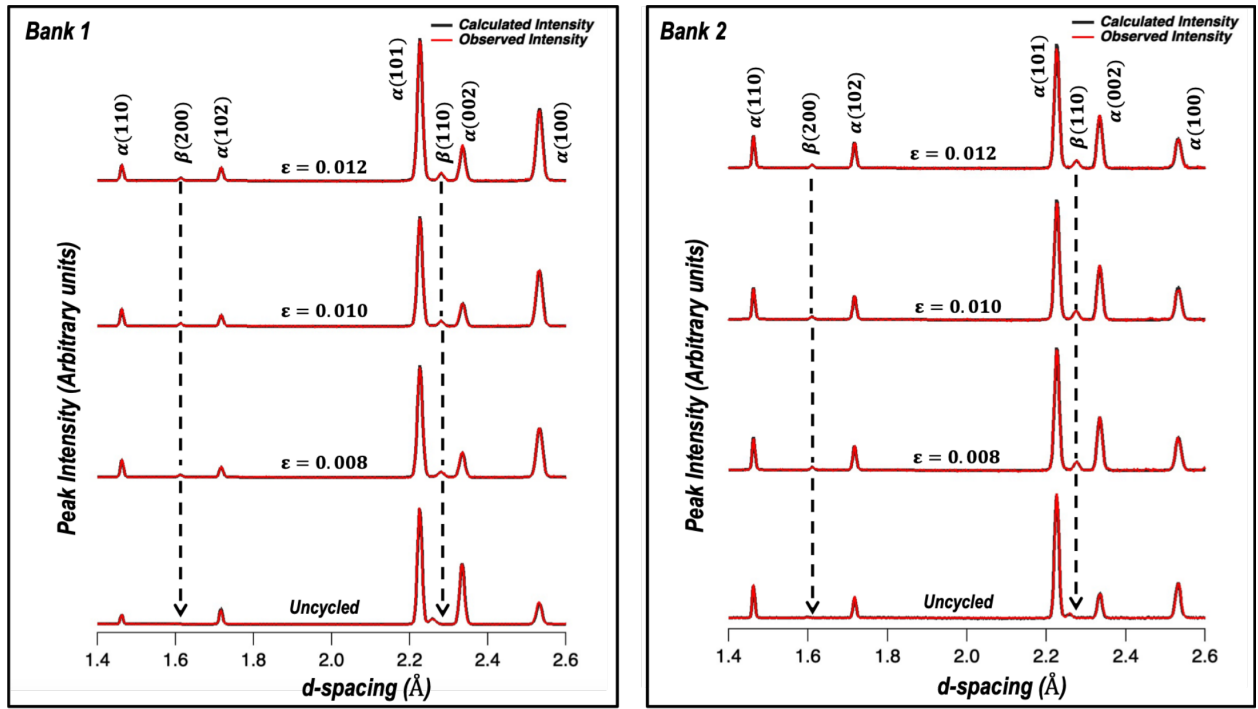


Figure 4.6: Intensity versus d-spacing plots showing the shift in the $\beta(110)$ peak in the thermo-mechanically cycled samples from Bank1 and Bank2.

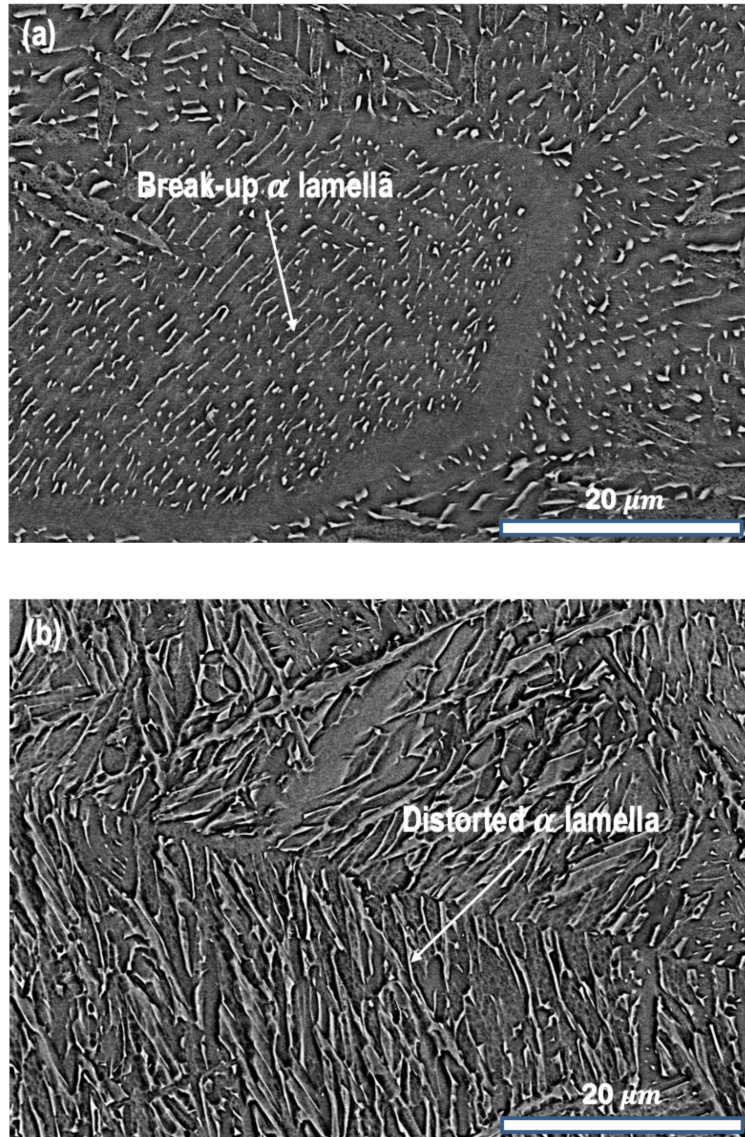


Figure 4.7: SEM Images across the gauge section showing the two distinct α/β morphologies; (a) A break-up of the lamellar α into finer sections with Vanadium enriched β ribs; (b) The distorted structure of the α phase.

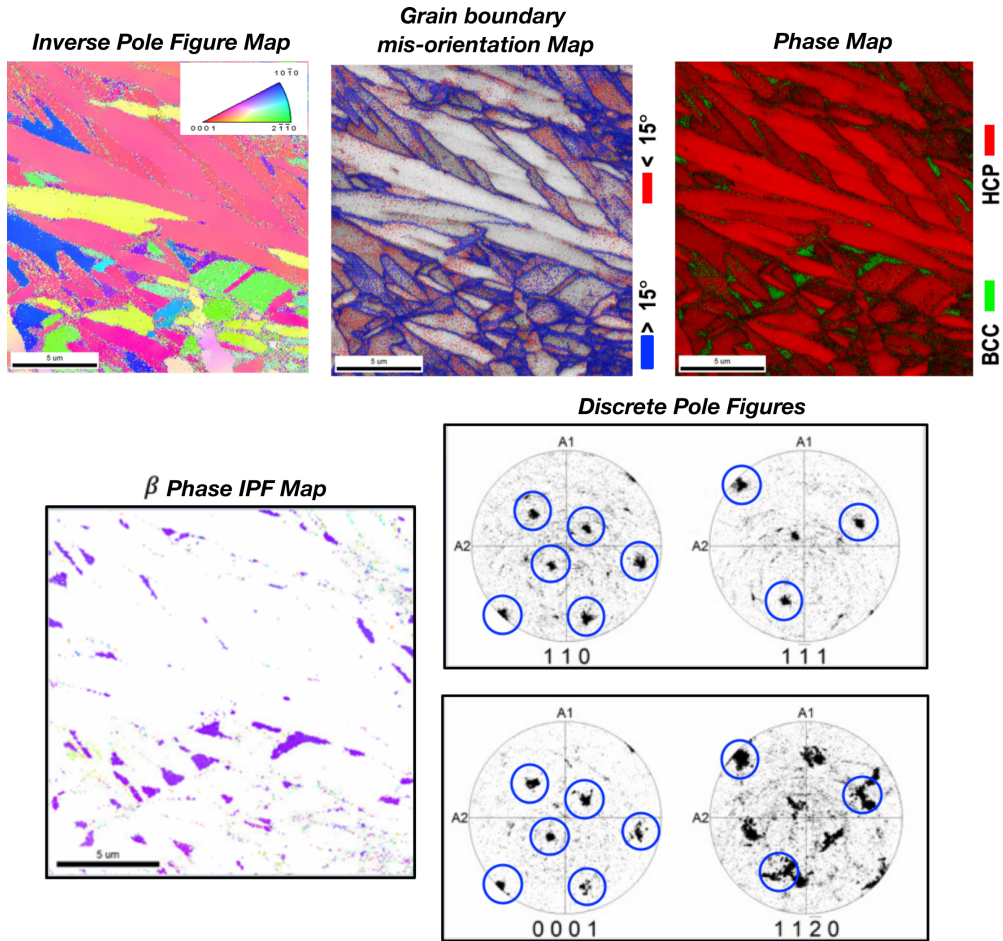


Figure 4.8: (Top) EBSD results comprising of the IPF maps, grain misorientation maps, phase map across the gage section; (Bottom) Extracted BCC IPF map and corresponding discrete pole figure plots indicating common poles between the α and β phases.

within regions of the β phase. Taking a closer look at the β , where the β grains alone were extracted from the IPF map, discrete pole figure plots were calculated. Common pole were noticed across the $\beta(110)$ and $\alpha(0001)$ planes and also from the $\beta[111]$ and $\alpha[11\bar{2}0]$ directions. This indicates that the growth of the β phase occurred while maintaining strong BO relationship. From this analysis, it can be inferred that the spike in the BCC β peak that we notice in our diffraction data, is not just a consequence of the texture alone, but from the strain accumulation due to thermo-mechanical reversals.

4.3 In-situ Neutron Diffraction experiments (Slow Thermo-mechanical reversals)

4.3.1 *Thermo-mechanical setup at VUCLAN beamline, SNS*

In-situ experiments at the VULCAN beamline was conducted to measure the temporal transients of plastic strain partitioning to the phases and the dynamic phase transformation kinetics during thermo-mechanical reversals. AM fabricated cylindrical samples were cut to the beamline specimen dimension of 8mm diameter and a length of 110mm. The diffraction setup at the beamline has been discussed in detail in the earlier section 4.1.2. The VULCAN beamline is equipped with an MTS load frame and induction heating coil on which the thermo-mechanical cycles were run. Special care needed to be taken particularly for our experimental design because of the following reasons. First, titanium has a negative scattering length (-3.44×10^{-15} m) in neutron coherent scattering while most of the alloying elements have a positive value which neutralizes the total scattering length. As a result, titanium alloys usually exhibit weak neutron scattering ability, and hence long exposure time or a large time bin of continuous data was required to achieve sufficient statistics in

the neutron diffraction pattern. Secondly, the high temperature extensometer could not be used for an accurate strain control; specifically, it is not designed for such high strain rates going back and forth in compression and tension alternatively in this experiment. Thus, displacement control was used instead, and the extensometer measured the strain during the in-situ experiment. Therefore, a slight modification, to our thermo-mechanical experimental setup had to be made in order to get good statistics. An initial measurement of the samples with a 1-hour exposure time was conducted before TM cycling to ascertain the initial characteristics of the α and β phases. As shown in [Figure 4.9](#), ‘n’ number of TM cycles were conducted following which the samples were held at 400 °C for an exposure time of 1-hour, followed by ‘n’ TM cycles. Thermal rates were maintained at 5 °C/s on heating and 1 °C/s on cooling.

4.3.2 *Results of the In-situ Thermo-mechanical reversals*

Although, we confirmed the dynamic phase transformation experiments in the earlier section, our desire was to analyze the changes in phase fraction as a function of thermo-mechanical cycling under in-situ conditions. Therefore, in-situ experiments were performed at the Vulcan beamline. Since modifications were made to the experimental set, one distinct feature that can be noticed from the stress versus time plot, marked by arrows in [Figure 4.9\(a\)](#), is the significant amount of stress relaxation that occurred at every isothermal 1-hour hold period at 400 °C. As an overall effect, we do notice the softening behavior from the hysteresis curve, shown in [Figure 4.9\(b\)](#). Diffraction peak analysis of the as-processed sample was performed prior to cycling. Analysis of the peak intensities show an initial reading of $97.29 \pm 0.2\%$ and $97.39 \pm 0.2\%$ of the α phase from Bank 1 and Bank 2 respectively. The corresponding β phase measured to be $2.71 \pm 0.2\%$ and $2.61 \pm 0.2\%$ from Bank 1 and Bank 2 respectively. Phase fractions and lattice parameters of the individual phases are summarized in [Table 4.2](#).

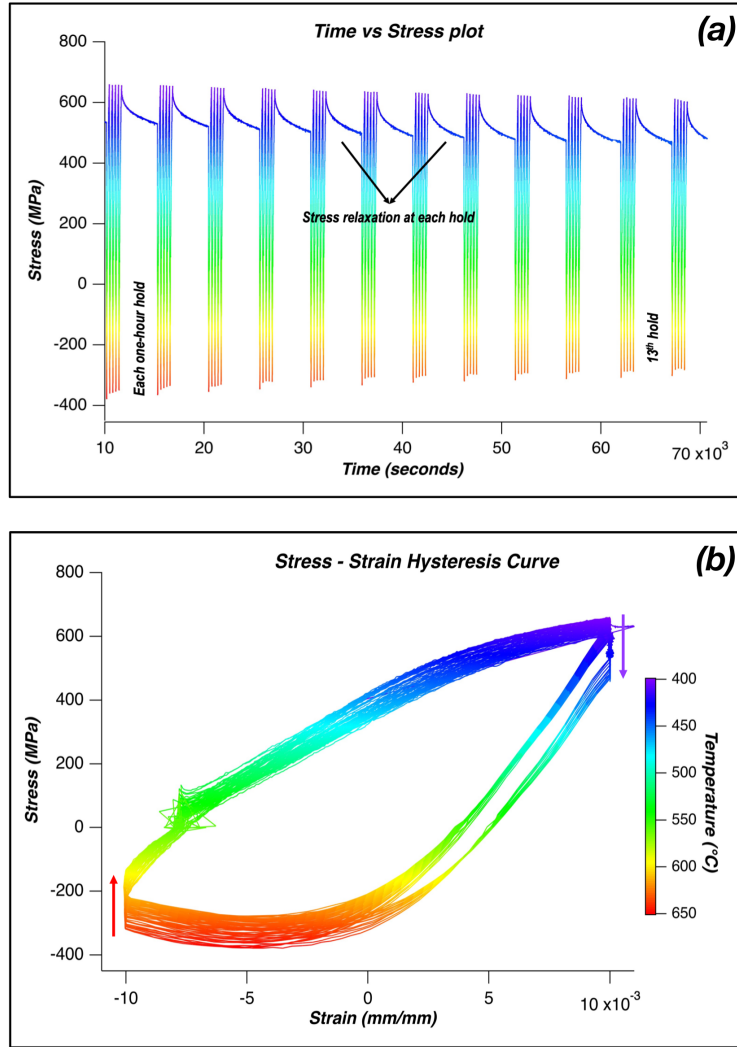


Figure 4.9: (Top) Stress versus Time plot showing the stress relaxation at every 1-hour hold period between cycles; (bottom) Hysteresis Stress-Strain curve of the in-situ thermo-mechanical test at the Vulcan Beamline, SNS.

Contour plots of the evolution of the two phases during thermo-mechanical cycling is shown in [Figure 4.10](#). From the peak intensities, it can be seen that as Bank 1 measures the compressive strain component, and Bank 2 simultaneously measures the tensile strain in each individual (hkl) peak. A magnified view of the first 5 cycles is shown in [Figure 4.10](#) marked by a red box. The peak intensity in these contour plots are a function of both the temperature and the mechanical strains. Analysis of the peak intensities from both the banks gives us information on the changes in phase fraction of the individual phases, the strain in each phase and qualitative information on the texture evolution. It should be pointed out that the overall signal peak intensity of Bank 2 is relatively poorer than Bank 1. This is because the neutrons collected by Bank 2 are the transmitted neutrons, whereas Bank 1 collects the reflected neutrons. However, analysis from both the Banks is crucial for understanding the phase kinetics.

4.3.3 *Phase fraction and Texture Analysis*

Rietveld Refinement using the GSAS software was done to extract phase fraction values and corresponding lattice parameters of the individual phases. Phase fractions values of the α and β phase from the initial state, Hold-1 and Hold-13 are tabulated in [Table 4.2](#). Data is inferred from an integration of diffraction neutrons over the 1-hour hold period (although significant softening was noticed during this hold period). Therefore, in the further text, each hold of 60min is referred to as ‘Hold-n’ (where n= 1-13). From the table, we can see that in both the banks there is an initial increase in the β phase fraction from $2.71 \pm 0.2\%$ to $9.51 \pm 0.9\%$ in Bank 1 and $2.61 \pm 0.2\%$ to $9.19 \pm 0.8\%$ in Bank 2, with a corresponding decrease in the α phase fraction. Although the samples were subject to lower temperature and strain rates, the increase in the β phase fraction is noticed with a corresponding shift in the lattice parameter, as in the case of our ex-situ rapid TM reversal experiments. Interestingly, at the

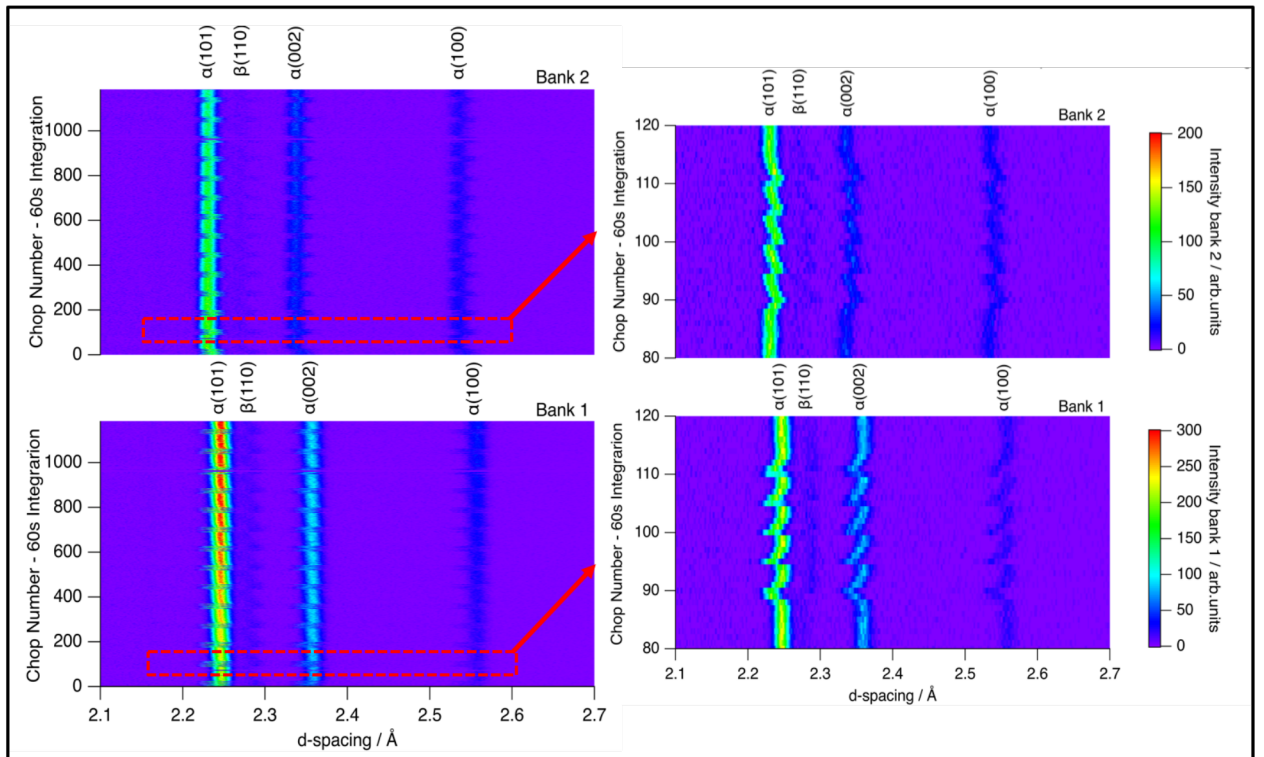


Figure 4.10: Contour plots of the in-situ thermo-mechanical cycle from both Bank1 and Bank2; on the right is a magnified image of one set of cycling (the color corresponds to the peak intensity).

<i>Diffraction Banks</i> <i>& Conditions</i>		<i>Exp. α</i> <i>Fraction</i>	<i>α Lattice</i> <i>Parameters</i>	<i>Exp. β</i> <i>Fraction</i>	<i>β Lattice</i> <i>Parameters</i>
<i>Bank 1</i>	<i>Initial d_0</i>	$97.29 \pm 0.2 \%$	$a_0 = 2.92$ $c = 4.66$ $c/a = 1.595$	$2.71 \pm 0.2 \%$	$a_0 = 3.19$
	<i>After 1st 5cycles</i> <i>(Hold 1)</i>	$90.49 \pm 0.9 \%$	$a_0 = 2.95$ $c = 4.74$ $c/a = 1.606$	$9.51 \pm 0.9 \%$	$a_0 = 3.23$
	<i>After 75cycles</i> <i>(Hold 13)</i>	$97.88 \pm 0.8 \%$	$a_0 = 2.95$ $c = 4.76$ $c/a = 1.603$	$2.10 \pm 0.8 \%$	$a_0 = 3.23$
<i>Bank 2</i>	<i>Initial d_0</i>	$97.39 \pm 0.2 \%$	$a_0 = 2.92$ $c = 4.66$ $c/a = 1.595$	$2.61 \pm 0.2 \%$	$a_0 = 3.19$
	<i>After 1st 5cycles</i> <i>(Hold 1)</i>	$90.81 \pm 0.8 \%$	$a_0 = 2.92$ $c = 4.66$ $c/a = 1.590$	$9.19 \pm 0.8 \%$	$a_0 = 3.21$
	<i>After 75cycles</i> <i>(Hold 13)</i>	$97.36 \pm 0.9 \%$	$a_0 = 2.92$ $c = 4.66$ $c/a = 1.590$	$2.63 \pm 0.9 \%$	$a_0 = 3.21$

Table 4.2: α and β phase fractions and lattice parameters calculated during in-situ slow thermo-mechanical cycles - before cycling at RT, after 5cycles and after 75cycles.

very end of the thermo-mechanical cycling, seen from Hold-13 the α and β phase fractions flipped. From our initial spike in the β phase fraction noticed at Hold-1 after 5 cycles, the subsequent cycles and one-hour hold periods altered the dynamic phase evolution. Analysis of Hold-13 shows a noticeable reduction in the β phase fraction from $9.51 \pm 0.9\%$ to $2.10 \pm 0.8\%$ and from $9.19 \pm 0.8\%$ to $2.63 \pm 0.9\%$ in Bank 1 and Bank 2 respectively.

Crystallographic texture in metallic AM parts arise due to the presence of solidification texture (i.e., columnar β grains that forms due to directional solidification) which is followed by the solid-state phase transformation of β to α with preferred crystallographic orientation relationship (i.e., the Burger's orientation relationship). The texture of α will influence the mechanical properties of the alloy drastically [140]. To evaluate the texture, the peak intensities of the primary α peaks are analyzed, namely the $\alpha(100)$, $\alpha(002)$ and the $\alpha(101)$ peaks from both detector banks. Intensities of the peaks from the Hold-1 (blue line) and the Hold-13 (red line), in Bank 1 and Bank 2 are compared as shown Figure 4.11. From the intensity plot, it can be seen that there exists a hierarchy of α peaks intensities, i.e., the $\alpha(100)$, (002) , (101) , (102) , (110) , (103) , (200) , (112) and (201) peaks. On comparing Hold-1 (after 5 cycles) and Hold-13 (after 70 cycles), it is noticed that there is a change in the texture as seen from the intensity of α peaks from Bank 1 and Bank 2, marked by the arrows. For instance, looking particularly at the $\alpha(101)$ peak intensity in Bank 1 started off with a high intensity and towards the end of the cycling, from Hold-13, one can notice the decreased peak intensity of the $\alpha(101)$ peak. On the other hand, there is a concomitant opposite trend noticed with the $\alpha(101)$ peak in Bank 2. Similar trend can be noticed in the minor α peaks of (102) , (110) , (103) and (200) too.

Although we do see a change in texture from the two banks, it is impossible to quantify this texture as the diffracted neutrons are collected only along the longitudinal and transverse direction (that is Bank 1 and Bank 2), with no rotation about the azimuth, and this is

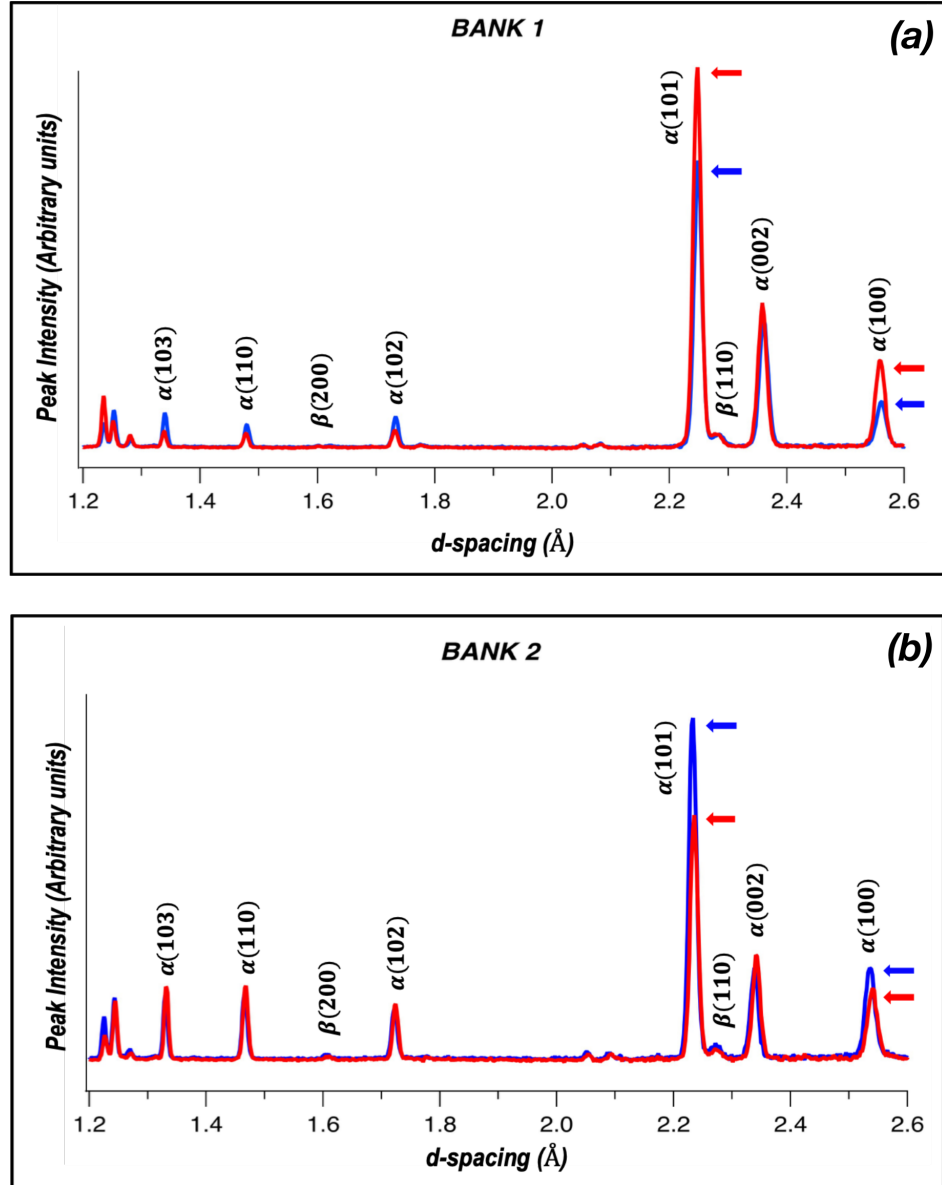


Figure 4.11: Qualitative Texture evolution, done as a comparison of the peak intensities from Hold-1 and Hold-13, due to the fluctuating thermo-mechanical gradients, denoted by the red and blue arrows.

not indicative of the texture of the entire region. Nevertheless, the current data gives us a qualitative result of the texture change that occurs when subject to thermo-mechanical gyrations.

4.3.4 *Microstructural characterization*

Although the in-situ experiments were successful, the rates used for the Gleeble[®] and neutron experiments are different. Therefore, it is of interest to compare the microstructures from both samples. The analysis from the gauge section of the in-situ samples was done and is shown in [Figure 4.12](#). Similar to the microstructure from the Gleeble[®] samples, there were regions of the break-up α and the distorted α morphology.

In addition to these α microstructures, a closer examination of the α phase revealed a “diffused α ” morphology. This “diffused α ” has been reported before by Ding et al [[139](#)]. The diffused α morphology is different from the other α structures, such that it looks like regions of small pockets, magnified in [Figure 4.12\(a\)](#) and (b). There were significant regions of this α morphology at the gauge section. This diffused α structure is known to be a high temperature α morphology that was partially dissolved into the β matrix but has not completely dissolved and has eventually been retained at room temperature. Interestingly, this kind of α morphology has not been researched before and its contribution to the mechanical integrity of the alloy is not known. The diffused α morphology has a polygonal shape, and no distinct sub-structure can be noticed.

4.4 Discussion

Although extensive research has been conducted in the fabrication and characterization of E-PBF Ti-6Al-4V, the phase kinetics under fluctuating thermo-mechanical reversals has

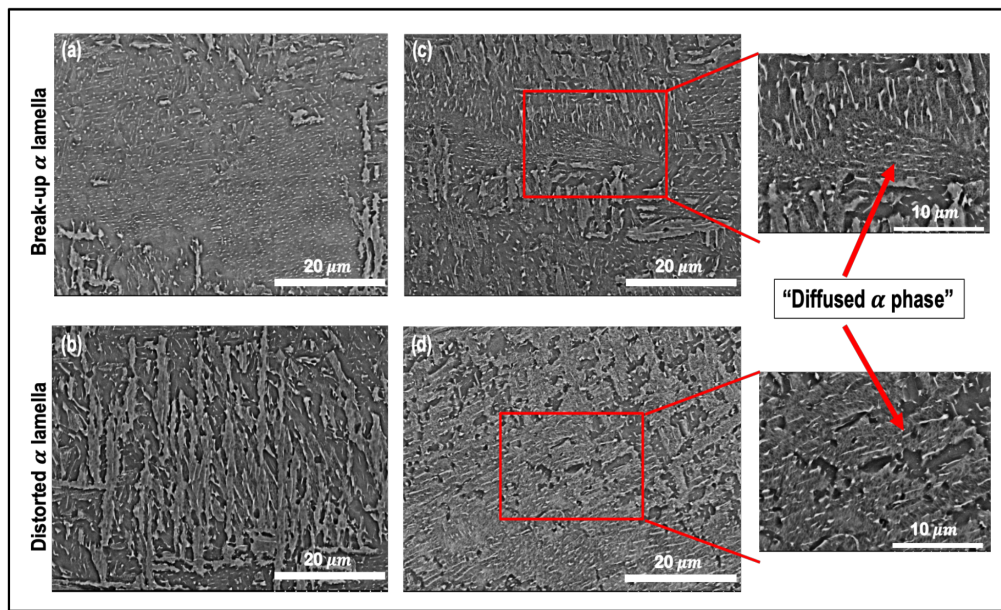


Figure 4.12: SEM imaging of the gauge section where similar regions of the 'break-up' α and distorted α were noticed; Diffused α morphology with a magnified view of the α structure.

not been addressed before. Our results appear to provide additional perspectives with reference to phase stability under cyclic thermo-mechanical gradients. Results from our controlled experiments have confirmed the following phenomena with reference to Ti6Al4V: (a) Rapid (30 seconds/cycle) and complete plastic strain reversals (tensile/compressive) lead to softening and stress relaxation. This softening is associated with an increase in β phase fraction; (b) During slow (300 seconds/cycle) TM reversals, the stress relaxation of the samples was accompanied with an increase in α phase fraction and changes to crystallographic texture. Since, we have two contrasting thermo-mechanical signatures, our results are rationalized based on published results and our new analysis under two sub-sections of ‘rapid temperature and strain reversals’ and ‘slow temperature and strain reversals’.

4.4.1 Rationalization of β phase increase during RAPID thermo-mechanical reversals

Softening was noticed in all the samples subject to rapid thermo-mechanical cycling in the Gleeble[®] experiments. From our results, a closer look at this behavior revealed an increase in the β phase fraction. This increase in the β phase can be accounted for by a variety of factors. In our experiments, there is a complex interaction between the temperature, mechanical loads and thermal rates, which could all have an influence on the β phase. Many of the individual components of these behaviors has been studied before and the following mechanisms can be put forth.

Thermodynamic Stabilization of the β phase:

An increase in the β phase fraction, of about 10% in the stressed state, after being subject to a uni-axial tensile load at 1000 °C has been reported by Koike et al before, for an $\alpha+\beta$ Ti-Al-Fe alloy [86]. In their study, tensile tests were conducted at various temperatures

which resulted in an increase in the β phase due to the presence of a localized elastic stress field, which was estimated to be around ~ 500 J/mole in the α phase. This hypothesis is evaluated using ThermoCalc[®] software and TCTI2 thermodynamic data base and is shown in Figure 4.13 [141]. In these calculations, the stability of α phase was first increased by reducing the molar Gibbs free energy of this phase by -200 J/mole with reference to β phase. This value was chosen based on typical stored strain energy that is expected due to displacive transformations or accumulated plastic strains [142]. Then, energy in increments of 25 J/mole was added to the α phase. As a result, the calculations arrive at 0 J/mole, which is the reference state. Then, the stability of α phase was decreased by adding +200 J/mole in increments of 25 J/mole. As expected, reducing the stability of the α phase leads to an increase in β phase fraction. Interestingly, our neutron diffraction measurements of the rapid TM cycled samples straddle these calculated β phase fractions.

Reduction of α/β growth rate due to accumulated plastic strain in β :

It is well known that the growth of β phase occurs by the diffusion of the alloying elements, specifically at the expense of the α phase rejecting vanadium. Since the vanadium content in α is almost constant up to the β -transus temperature, the rate controlling factor for the growth of the β phase is the partitioning of vanadium to the β phase [143].

The diffusivity of vanadium in the β phase at 400 °C is calculated to be many orders of magnitude (10^{-18} m²/s, when compared to the diffusivity of Vanadium in β at 1000 °C of 10^{-14} m²/s) slow. However, the diffusivity into the β phase can be increased if dislocations are generated at the α/β interface via pipe diffusion [144]. Although we do not have any direct evidence for the generation of the dislocations at the interface at this time (refer Sec.5.3.4), full-width-at-half-max analysis from our neutron diffraction measurements indicated an increase in FWHM values. As noted earlier, there was a noticeable shift in the lattice parameter of the $\beta(110)$ peak indicating a strain of 0.6% accumulated in the β phase.

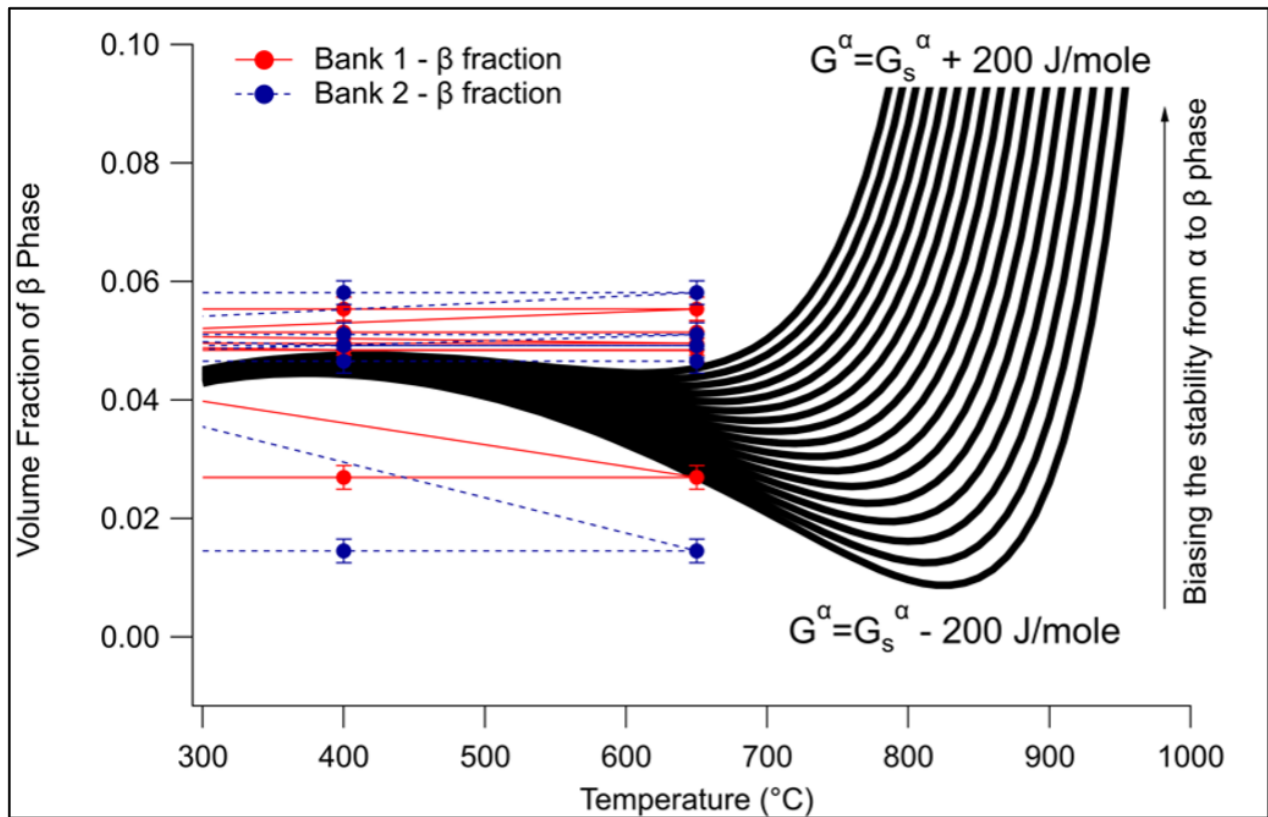


Figure 4.13: Predicted variations of β phase fraction as a function of temperature with step-by-step changes to stability of α phase at increments of 25 J/mole moving from highly stable (-200 J/mole) to highly unstable (+200 J/mole) conditions.

Interestingly, although the β phase fraction is small, it is evident that strain accumulation is much more prevalent in the β phase. This phenomenon can be explained by looking at the critical resolved shear stress (CRSS) in the two phases. Literature has shown that basal and prismatic planes are the more dominant slip systems in a two-phase titanium alloy [145] [132]. Seemingly so, since the phase fraction of the α phase is 90%, there is a higher chance of the α phase to strain, possibly so at the initial stages. On the other hand, literature has shown there is a preferential texture alignment of the α and β grains in AM. Prior β grains have a strong $\langle 001 \rangle$ texture parallel to the build direction [132]. Therefore, the resulting α grains preferentially grow following a Burgers orientation, which is $(0001) \parallel (110)$ and $\langle 11-20 \rangle \parallel \langle 111 \rangle$. With this highly dictated orientation, and the loading axis along the $\langle 001 \rangle$, slip is constrained in the basal and prismatic slip systems of the α phase. Whereas, in the β phase, slip can be easily activated in the $(110) \langle 111 \rangle$ slip system. Thus, although the β phase is the minor phase, owing to the CRSS, it will be easier to accumulate strains in the β phase. In addition, the accelerated stress relaxation at 400 °C on additional thermo-mechanical cycling supports this hypothesis. The key requirement for this hypothesis is that the interface motion should be faster than the stress relaxation that usually reduces the defect density.

Formation of new strain free β phase:

It is known from literature that, through the Burgers orientation relationship, the α phase nucleates 12 variants from the β phase on cooling. Likewise, the β phase can also form 6 different variants from the α phase on heating. In AM of Ti6Al4V, the first phase to form on cooling irrespective of the geometry, at such high cooling rates of about 8.6×10^4 °C/s, is the martensitic α' phase. This α' phase is a heavily faulted structure with a high dislocation density [146]. On further thermal cycles, this α' is known to decompose to the α -primary + β phases. At temperatures below 600 °C, Gil Mur et al. has shown that the α' doesn't

fully decompose [147]. In our builds, a pre-heat temperature of about 475 °C is maintained throughout the build, which is quite a low temperature, and therefore there could be a possibility that not all the α' decomposes. In Ti6Al4V, α' is known to decompose via nucleation of the β phase on the twins and dislocations [146]. In their study on the phase transformation pathway during cooling in Ti-6Al-4V, Nandwana et al. has shown that, α' first nucleates from the β grain following the BO relationship on cooling [70] [101]. On further decomposition, α' heterogeneously nucleates different β variants. Ideally, there are 6 variants of β that can form from an α grain, obeying the BO relationship. Since the α' is a highly faulted structure, the large number of dislocations and faults in the α' structure act as potential nucleation sites for the β phase. Therefore, it is possible that during thermo-mechanical cycling, the deformation structures in the α' phase led to the nucleation of a new β phase. Gao et al. has also shown in his thermodynamic calculations that during thermo-mechanical loading, the β phase fraction increases by the heavily distorted α phase, causing a local rearrangement of atoms to occur, leading to the nucleation of the β phase [82]. Further, in the presence of deformation structures within the β grain, the driving force for the growth of the β phase via diffusion of Vanadium through the dislocations, that is pipe diffusion, will be enhanced. Our study, therefore, gives insight to the underlying possible mechanisms playing a role in the kinetics of phases subject to cyclic thermo-mechanical signatures.

4.4.2 *Rationalization of the α phase formation during SLOW thermo-mechanical reversals*

In contrast to the rapid thermo-mechanical gyrations, with the slow thermo-mechanical gyrations, each hold period of 1 hour in between cycles altered the shape of the stress-strain curve and the phase transformation kinetics. One of the distinct features to note is the

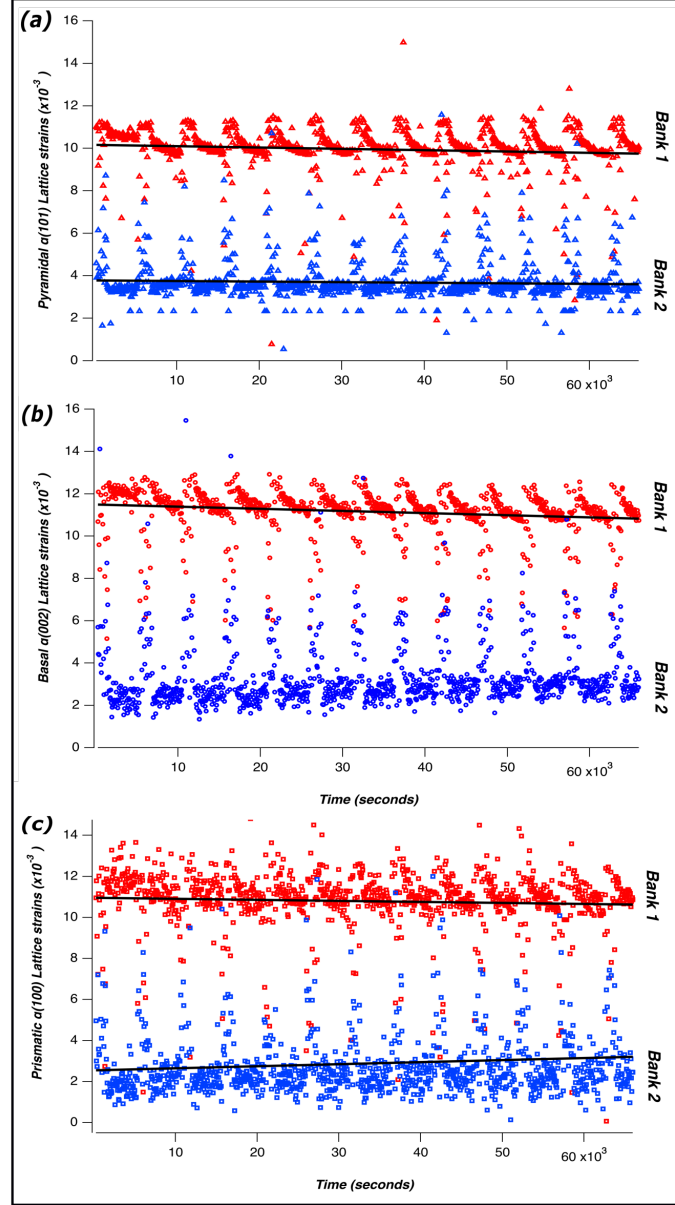


Figure 4.14: Plot of the lattice strains in the $\alpha(101)$ Pyramidal plane (top), $\alpha(002)$ Basal plane (mid), $\alpha(100)$ Prismatic planes (bottom) from Bank1 (marked in red) and Bank2 (marked in blue).

drastic stress relaxation at every isothermal 1-hour hold period, with a subsequent increase in the α phase fraction. The rationale behind this phase transformation is put forth below.

Strain Accumulation in the α phase:

One of the key questions that arises from the above texture is whether this variant selection is based on elastic stress fields or due to the presence of accumulated plastic strain that impede the growth of certain variants. Elastic lattice strains in the α phase was calculated using equation 1 also plotted in [Figure 4.14](#). The individual strains were calculated from the change in the d-spacing with reference to the initial d_0 measurement. The red symbols indicate the data from Bank1 and the blue symbols from Bank2. The basal plane $\alpha(002)$ and the pyramidal plane $\alpha(101)$ show the maximum effects of strain relaxation at every hold period. Data points from the prismatic plane $\alpha(100)$, were noisy and no specific trend could be delineated. It was difficult to pick out the effect of the lattice strains on the β phase, due to the large noise to signal ratio. This is indeed expected for the following three reasons: (a) the volume fraction of β phase is small; (b) the integration time for measurement is also low; (c) titanium is a weak scatterer of neutrons. Therefore, we cannot comment on the entirety of the elastic and plastic strain distributions within α and β phases. However, the analyses show that under thermo-mechanical gyrations, there is complex elastic and plastic strain distributions between the α and β phases. Stress relaxation phenomena post hot compression test in AM Ti6Al4V has been reported before by Wang et al, and they conclude that there was no phase transformation involved, but rather a defect accumulation in the α phase as high temperature deformation mechanisms, such as climb and glide activate in the α phase [148]. This can be further verified from the lattice strains, where the maximum stress relaxation occurred in the α planes.

Reverse transformation trend ($\beta \rightarrow \alpha$):

In addition to the stress relaxation, an overall increase in the α phase fraction is noticed.

This phenomenon has been reported before, where post deformation, a reverse transformation occurred where the meta-stable β phase transforms back to the α phase on isothermal holds post deformation [83] [85]. As seen from Table 4.2, after the first 5 cycles (Hold-1) showed an increase in the β phase. But subsequently, towards the end, the α phase stabilized. In their study, Goa et al has shown that alongside a stress relaxation, post deformation, there was an increase in the α phase fraction. Since the newly formed β grains are not thermodynamically stable, they tend to transform back to the more stable state, which is the α phase at 400 °C. The driving force for this transformation is the Gibb's Free Energy difference between the α and β phases. In our case, the 1-hour hold period at isothermal temperature of 400 °C after every 5 thermo-mechanical cycles, led the increased β phase fraction that resulted from dynamic transformations during cycling to transform back to α . Therefore, leading to an increase in the α phase fraction towards the end.

4.5 Summary of chapter

This chapter can be summarized as:

(1) Our cyclic thermo-mechanical testing on Ti6Al4V alloy confirmed that the flow properties and associated dynamic phase transformation ($\alpha \leftrightarrow \beta \leftrightarrow \alpha$) are different from monotonic and history independent assumptions used by computational modelling literature.

(2) Out-of-phase cyclic thermo-mechanical cycles between 400 °C to 650 °C, with alternating compressive and tensile strain amplitudes of 0.8%, 1% and 1.% showed stress-strain hysteresis for Ti6Al4V with symmetric progressive softening of 370 MPa over 75 cycles, which is higher than the published literature on thermo-mechanical fatigue testing done at a lower temperature range.

(3) The observed flow properties are correlated to phase fractions measured by neutron diffraction. Samples subjected to rapid TM (30 seconds/cycle) reversals showed a monotonic increase in the β phase fraction of about 5% in comparison to our reference sample. In contrast, slow TM (300 seconds/cycle) reversals showed unexpected nonlinear behavior of initial increase of β phase fraction followed by decrease.

(4) The above differences are attributed to relative strain partitioning between α and β phases and subsequent recrystallization derived through diffraction peak width analyses. From the peak analysis of the rapid thermo-mechanical reversals (at room temperature), we notice an increase in the dislocation density in the β phase, which further laid the pathway for pipe diffusion to have occurred. The slow thermo-mechanical reversals depicted a bias in the dislocation spread in the β grains, where only certain β grains, whose orientations were preferentially aligned with respect to the loading direction, carried the load.

CHAPTER 5

Role of thermo-mechanical gyrations on α/β interface stability in AM Ti6Al4V

In the previous chapter, we observed progressive softening in Ti6Al4V alloy subjected to out-of-phase thermo-mechanical reversals between 400 °C and 650 °C, with a plastic strains alternating back and forth in tension and compression [133]. Neutron diffraction analysis indicated that the strain partitioning between the α and β phases was accompanied by dynamic $\alpha \leftrightarrow \beta$ phase transformation. In this chapter, the observed increase in the β phase fraction and its implications on the solute partitioning of Aluminum and Vanadium is further investigated at the nano-level scale with Atom Probe Tomography. The analysis of the α/β interface concentration profile resulted in a rationalization of the probable transformation pathway, whether reconstructive or displacive, of dynamic phase transformations during TM reversals. The details entailed in the chapter has been published in Scripta Materialia [149].

5.1 Experimental Setup

5.1.1 *Thermo-mechanical reversals*

Thermo-mechanical reversals were conducted on a Gleeble[®]3500. To further investigate the behavior of Ti6Al4V samples subject to TM reversals between 400 °C and 650 °C, with plastic strain limit of 0.010 mm/mm alternating between tension and compression, a batch of samples were subject to a certain number of TM reversals, i.e., 15cycles, 30cycles, 45cycles, 60cycles and 75cycles. This experimental plan was formulated to track the β phase evolution with respect to TM reversals. Once TM cycled at the Gleeble[®]simulator, phase fraction analysis on these samples were done with neutron diffraction. Neutron diffraction specifics are outlined in the previous chapter. Each sample was exposed to neutron for an exposure time of 1 hour. Analysis on these samples was done with reitveld refinement taking into account texture effects.

5.1.2 *Atom Probe Tomography*

Nano scale compositional analyses of the as-processed (0cycle) and gauge section of the 45cycles and 75cycles samples were performed with Atom Probe Tomography, at the Center for Nano-Phase Materials (CNMS), Oak Ridge National Lab. Site-specific milling of atom probe needles were prepared using the FEI Nova 200 dual beam equipment. FIB coupons were cut into individual nano-sized atom probe tips, electro-polished and sharpened to be about (800 x 250) nm in size. Atom Probe Tomography was performed using a CAMECA LEAP 4000X HR instrument. During the analyses the base temperature was maintained at 50K and controlled field evaporation was achieved with a 355nm laser wavelength with a 10ps pulse width. A pulse energy of 50-80 pJ was maintained to keep the $\text{Al}^+/\text{Al}^{++}$ mass peak

ratio at 10. The detection rate was set at 0.5% (1 atom per 200 pulses) at a frequency of 200kHz. A data set of 30M ions were collected, except the 45cycles samples was restricted to 5M ions because the interface was detected at an early stage. The properties of the α/β interfaces were extracted only from data sets with good statistical significance. The atom positions were then re-constructed and evaluated using the Image Visualization and Analysis Software (IVAS) 3.6. Proximity histogram (Proxigram) analysis were done across the interface to extract the concentration profile.

5.1.3 *TEM Characterization*

TEM analysis on the thermo-mechanically cycled sample is done in collaboration with the MURI team at OSU. The TEM lamella was prepared using a Nova Nanolab 600 (Formerly owned by FEI, now Thermo Fisher Scientific Inc.) dual beam scanning electron microscope (SEM). A pre thinned lamella with a protective Pt cap was trenched out using a focused Ga ion beam, operated at an accelerating voltage of 30kV. The lamella was then transferred onto a Cu-omni grid using a micromanipulator and thinned down to electron transparency by iteratively reducing the beam current from 0.92 nA to 28 pA at an operating voltage of 30kV. The TEM lamella was characterized using a Tecnai G2-30 TEM (Formerly FEI, now owned by Thermo Fisher Scientific Inc.) operated at an accelerating voltage of 300kV.

5.2 Mechanical Behavior and Interface Profile

5.2.1 *Stress-Strain response and Neutron Diffraction analysis*

Stress-Strain Hysteresis

The hysteresis stress-strain curve from the TM experiments is plotted [Figure 5.1](#). Each sample is subject to a specific number of TM cycles, i.e., 15, 30, 45 and 75 cycles. For a state

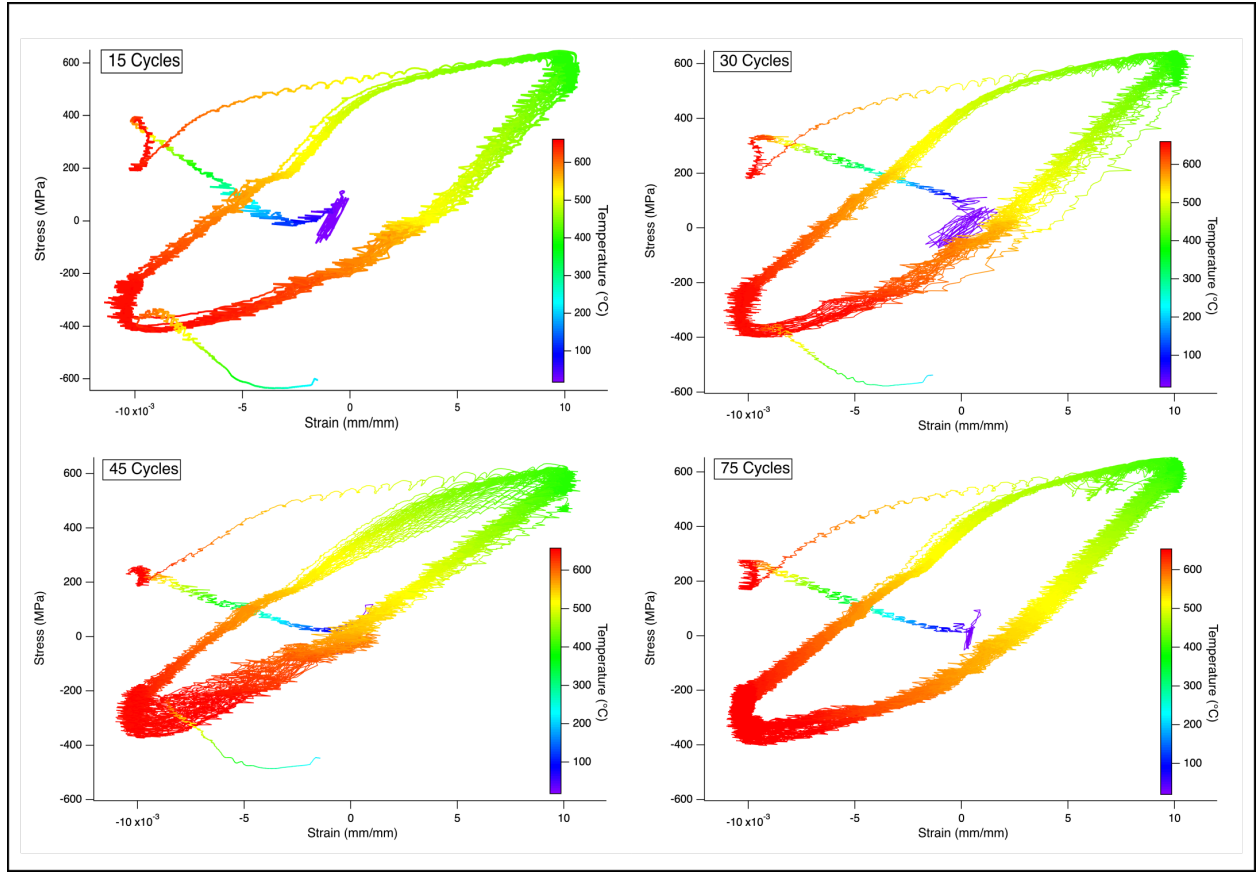


Figure 5.1: Hysteresis Stress-Strain plots of the thermo-mechanical reversals showing the 15cycles, 30cycles, 45cycles and 75cycles resulting in the softening behavior.

of reference to our experimental data, one sample from the same batch in the as-fabricated condition, subject to no cycling, is measured and analyzed and is hereafter referred to as the '0cycle' sample. The hysteresis stress-strain plot of all the TM cycled samples showed similar and consistent softening behavior, with an asymmetric stress level on the compressive and tensile sides. This asymmetry is reasonable as the stress-strain properties of any material are temperature dependent. At this point, it is noteworthy to mention that the in-phase TM cycling failed at the initial stage of cycling, due to the samples buckling. This is due to a greater compressive strain acting on a tensile strained gauge section. Therefore, all our TM cycles were run out-of-phase, i.e., compression on heating and tension on cooling (4.1.1). In this chapter, we will be focusing on 3 of these samples, the 0cycle, 45cycles and 75cycles samples, and they will be referred to as such throughout this chapter.

Neutron Diffraction To elucidate the dynamic phase transformation occurring due to TM reversals, α and β phase fractions of the TM samples was analyzed via neutron diffraction analysis at the Vulcan beamline. Each sample, after being TM cycled at the Gleeble® Simulator, is exposed to neutrons primarily over the gauge section (refer 4.1.2 for details on neutron diffraction), for an exposure time of 1-hour. Data analysis on these samples was done by integrating the diffracted neutrons collected over 60 min period. The intensity versus d-spacing plot for the 0cycle, 45cycles and 75 cycles is shown in Figure 5.2.

Notice the $\beta(110)$ peak in the 0cycle sample. The $\beta(110)$ peak being the first primary peak in the BCC system is a prime indication of the β phase in all our analysis. On the other hand, the three main α peaks namely the basal $\alpha(002)$, the prismatic $\alpha(100)$ and the pyramidal $\alpha(101)$ peaks are the prominent peaks of the α phase. Reitveld refinements of the data showed that the as fabricated 0cycle sample showed 97% α and 3% β (from

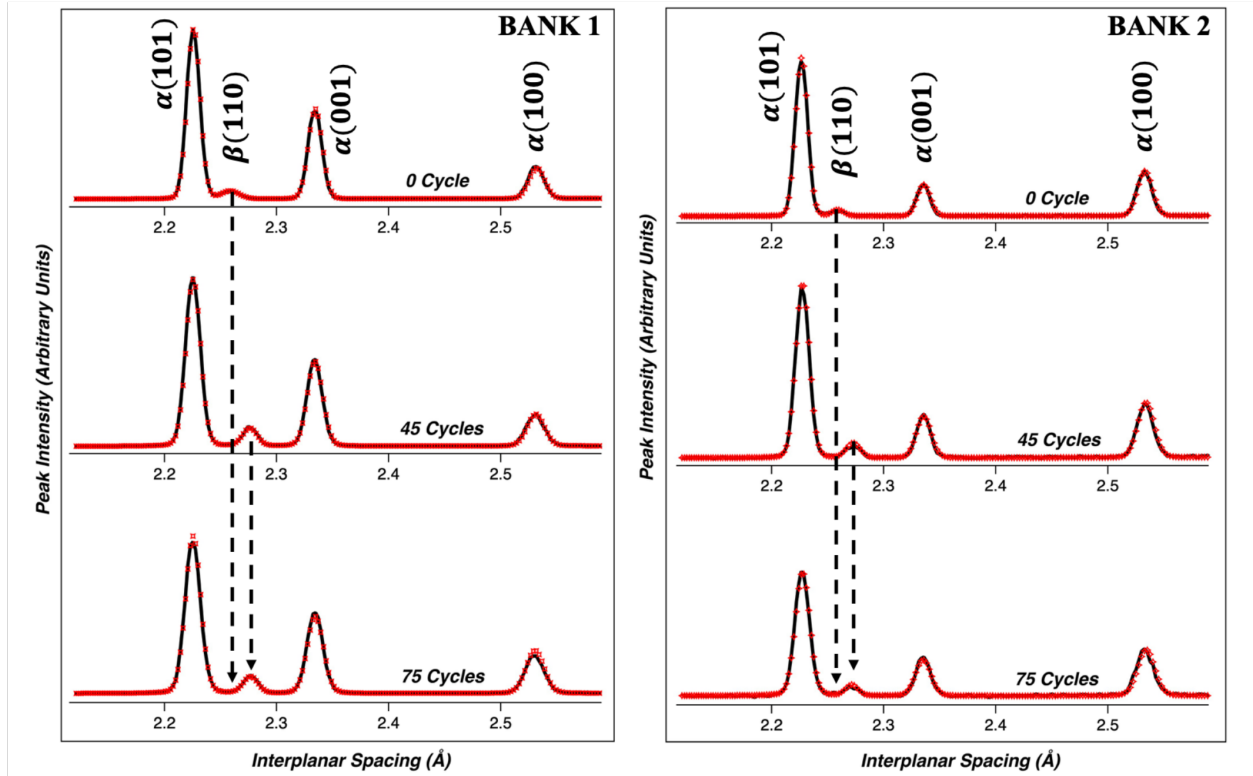


Figure 5.2: Neutron diffraction plots (peak intensity versus d-spacing) of the 0cycle, 45cycles and 75cycles. The black arrows highlight the shift in the $\beta(110)$ peak with reference to the 0cycle sample.

both Bank1 and Bank2). Comparing the intensity plot of the 0cycle samples to the thermo-mechanically cycled samples, 45cycle and 75cycle, a distinct spike in the $\beta(110)$ peak is noticed, which is indicative of an increase in the β phase fraction tabulated in [Table 5.1](#). The β phase fraction increase to about 5% in both the 45cycles and 75cycles sample. This increase in the β phase fraction indicates that macro scale TM fluctuations indeed has caused a change in the interface stability. A quantitative analysis of texture cannot be done from the peak intensities because it does not consider a whole rotation of the sample. But a rather qualitative analysis can be done by looking at the changed peak intensities of the minor α peaks. It can be concluded that straining occurs rather preferentially where the planes are aligned along particular directions to the loading conditions.

At this juncture, the dynamic strain partitioning between the α and β phases accompanied by an ($\alpha \leftrightarrow \beta$) phase transformation is delineated with neutron diffraction, where all the TM cycled samples indicated an increase in the β phase fraction. The observed change in β phase percentage (5%) with thermo-mechanical cycles was rather unexpected because thermodynamic equilibrium predicts negligible phase changes within that temperature range, as marked by the black triangles in [Figure 5.3\(a\)](#). Therefore, this led to the follow-up question on the phase transformation pathway observed as to whether the $\alpha \rightarrow \beta$ phase transformation occurred via a reconstructive mode or a displacive. A possible prediction of the phase transformation pathway can be explained by the solute partitioning of Al and V across the interface. As shown in [Figure 5.3\(b\)](#), ThermoCalc[®] indicate that phase transformations in Ti6Al4V between temperatures of 600 and 1300K, largely occurs by the partitioning of Vanadium. Hence, by tracking the changes in the Vanadium concentration in the α and β phases, insights into the transformation mode can be explained.

<i>Detector Bank</i>	<i>Bank 1</i>		<i>Bank 2</i>	
<i>No. of cycles/Phase</i>	$\alpha(\text{wt.}\%)$	$\beta(\text{wt.}\%)$	$\alpha(\text{wt.}\%)$	$\beta(\text{wt.}\%)$
<i>0 cycle</i>	97.3 ± 0.02	2.7 ± 0.05	98.5 ± 0.02	1.5 ± 0.04
<i>15 cycles</i>	95.0 ± 0.01	5.0 ± 0.04	94.8 ± 0.01	5.2 ± 0.03
<i>30 cycles</i>	95.2 ± 0.02	4.8 ± 0.04	95.1 ± 0.02	4.9 ± 0.02
<i>45 cycles</i>	94.5 ± 0.02	5.5 ± 0.05	94.2 ± 0.03	5.8 ± 0.04
<i>60 cycles</i>	95.0 ± 0.02	5.0 ± 0.03	94.9 ± 0.02	5.1 ± 0.05
<i>75 cycles</i>	94.9 ± 0.02	5.1 ± 0.04	95.3 ± 0.03	4.7 ± 0.03

Table 5.1: Measured α and β phase fraction values in the sequentially thermo-mechanically cycled samples indicating an increased β phase fraction in all the cycled samples.

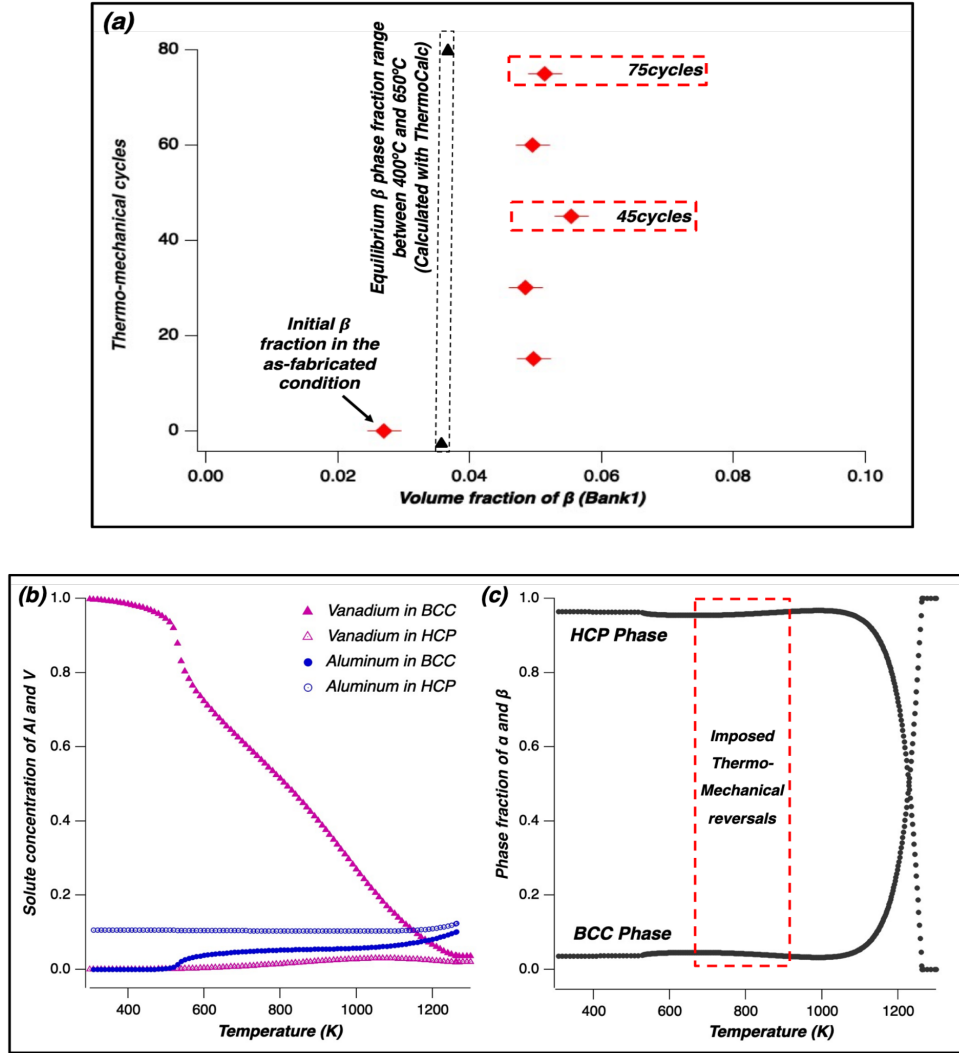


Figure 5.3: (a) Increase in the β phase fraction noticed in all the thermo-mechanically cycled samples when compared to the equivalent β phase fraction under thermodynamic equilibrium (marked by the boxed region between two triangle); (b) Change in solute concentrations in the α and β phases with temperature; (c) α and β phase fraction with temperature.

5.2.2 *Interface profile of reference sample*

The partitioning of aluminum and vanadium in between α and β phases is a crucial component to rationalize the phase transformation mechanism. Figure 5.4 shows the 3D atom maps of Ti, Al and V respectively of the 45cycles and 75cycles samples, across the α/β interfaces. A clear partitioning of the alloying elements is noticed, where Al (blue) partitions more to the α phase, and the V (pink) partitions to the β phase. The interface solute concentration profile from the as-processed sample (0cycle) is summarized in Figure 5.4

Quantitative analyses of the concentration profiles across the α/β interfaces were performed using proximity histograms (i.e., proxigram) analysis [150]. The analysis extended 20nm on either side of the α/β interface. As expected, Vanadium being a β stabilizer, there is a strong partitioning of Vanadium across the β lath. On the other hand, Aluminum, being a strong α stabilizer is seen to partition more in the α phase. In the as-processed condition, the measured vanadium concentration in the β phase is 30 at% and in the α phase 2.27 at%. Similarly, the measured aluminum concentration is 8 at% in the α phase and 2 at% in the β phase. These values are consistent with the reported literature on E-PBF of Ti6Al4V builds, where the Vanadium in the β phase was reported to be in the range of 25 – 28 at% [101, 151]. This high Vanadium content in the β phase, corresponding to an equilibrium temperature of around 570 °C calculated with ThermoCalc, indicates the final temperature at which the $\beta \rightarrow \alpha$ transformation was completed.

5.2.3 *Interface profile of the 45 and 75 cycles sample*

Similar analyses was performed on the 45 and 75 cycles samples, shown in Figure 5.5 and the interface concentration profile shown in Figure 5.6, where the vanadium concentration in the β phase was measured to be 18 at% and 17 at%, respectively. Details of other alloying

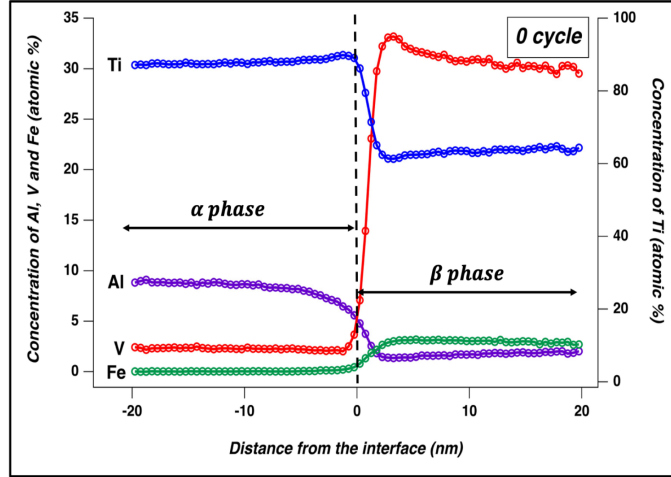
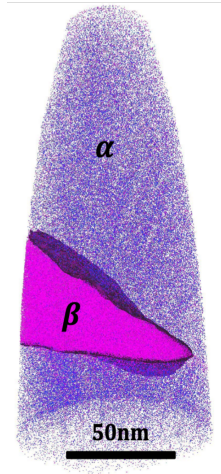
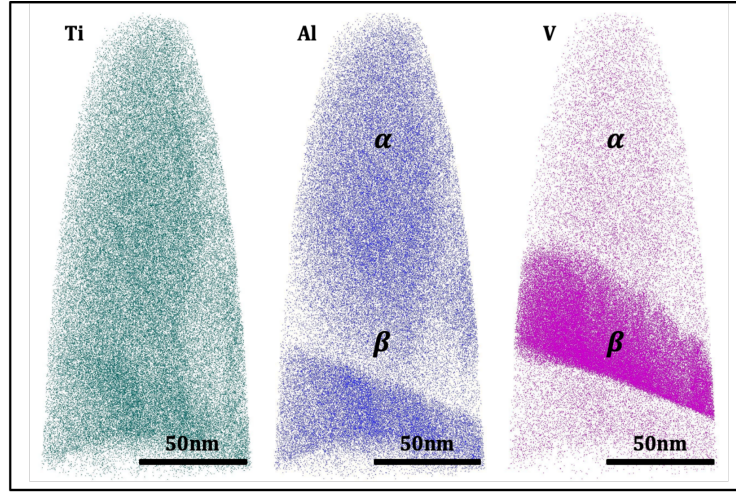


Figure 5.4: 3D reconstructed atom map emphasizing the interface between the α and β phase and the corresponding proximate histogram showing the atomic concentrations of Ti(blue), Al(purple), V(red) and Fe(green) across the interface (righthand scale bar denotes the concentration of Ti).

elements are tabulated in [Table 5.2](#). Negligible changes were observed in the aluminum content across both the phases. This reduced Vanadium concentration in the β phase confirms our neutron diffraction analysis indicating the increase in the β phase fraction and our hypothesis of a phase transformation being triggered during TM reversals. Neutron diffraction analysis showed that the β phase fraction almost doubled (2.5% in 0cycles to 5.7% in 45cycles) post thermo-mechanical reversals. This corresponded well with the simultaneous decrease in the Vanadium content of about an order of half (30 at% in the 0cycle to 18 at% in the 45cycles). In summary, a significant in the vanadium is redistributed in both the thermo-mechanically cycles (45 and 75cycles) samples, in comparison to the 0-cycle sample. In specific, the doubling of β phase fraction post thermo-mechanical reversals can only be sustained by the reduction of vanadium in the β phase.

5.3 Discussion

The results negated the prevailing hypothesis that dynamic transformations under thermo-mechanical reversals at low temperature could be displacive with no redistribution of alloying elements between the α and β phases [70, 146]. The concentration profile, as shown in [Figure 5.6](#), stipulates that a reconstructive mode of phase transformation is indeed significant to the emerging research on dynamic phase transformations [4, 22, 82]. The above results will be rationalized based on literature and computational thermodynamic models.

5.3.1 *Feasibility of displacive transformation*

To sustain the α to β phase displacive transformations, the temperature of the sample should be increased above the T-zero, i.e., temperature at which the molar Gibbs free energy of the α and β are the same ($G_\alpha = G_\beta$) for a given composition. The measured α composition in

<i>Phase</i>	<i>Solute Elements</i>	<i>0cycle (at.%)</i>	<i>45cycles (at.%)</i>	<i>75cycles (at.%)</i>
<i>α Phase</i>	<i>Ti</i>	87.9 ± 0.09	87.5 ± 0.43	85.1 ± 0.11
	<i>Al</i>	8.3 ± 0.08	8.5 ± 0.36	9.1 ± 0.09
	<i>V</i>	2.3 ± 0.04	2.8 ± 0.2	2.6 ± 0.05
	<i>Fe</i>	0.05 ± 0.02	0.10 ± 0.01	0.06 ± 0.01
	<i>O</i>	0.5 ± 0.02	0.4 ± 0.08	0.4 ± 0.02
<i>β Phase</i>	<i>Ti</i>	65.7 ± 0.18	74.7 ± 0.5	73.1 ± 0.10
	<i>Al</i>	2.19 ± 0.05	3.8 ± 0.2	4.8 ± 0.06
	<i>V</i>	29.0 ± 0.16	18.8 ± 0.5	17.7 ± 0.11
	<i>Fe</i>	2.8 ± 0.06	2.0 ± 0.1	1.7 ± 0.03
	<i>O</i>	0.09 ± 0.03	0.1 ± 0.04	0.1 ± 0.01

Table 5.2: Comparison of the solute concentrations across the α and β phases in the reference sample and the thermo-mechanically cycled samples, showing a decreased Vanadium concentration across the β phase in both thermo-mechanically cycled samples.

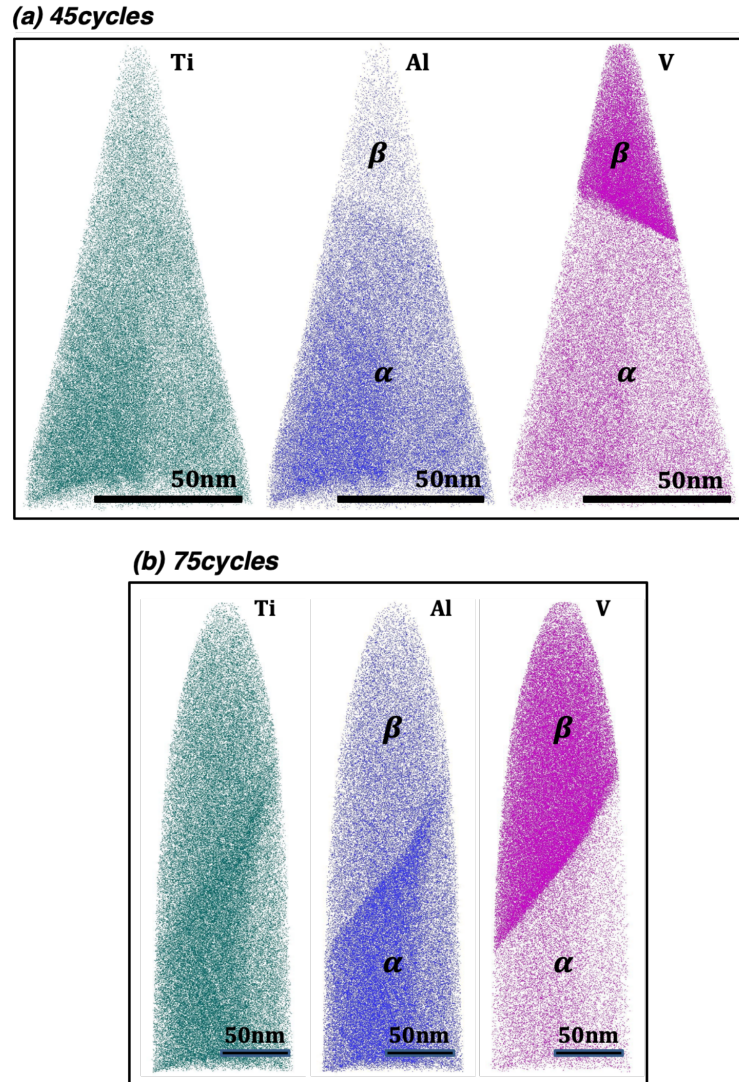


Figure 5.5: 3D reconstructed maps of Ti, Al and V in the thermo-mechanically cycled samples; (a) 45cycles and (b) 75cycles showing the α/β interface.

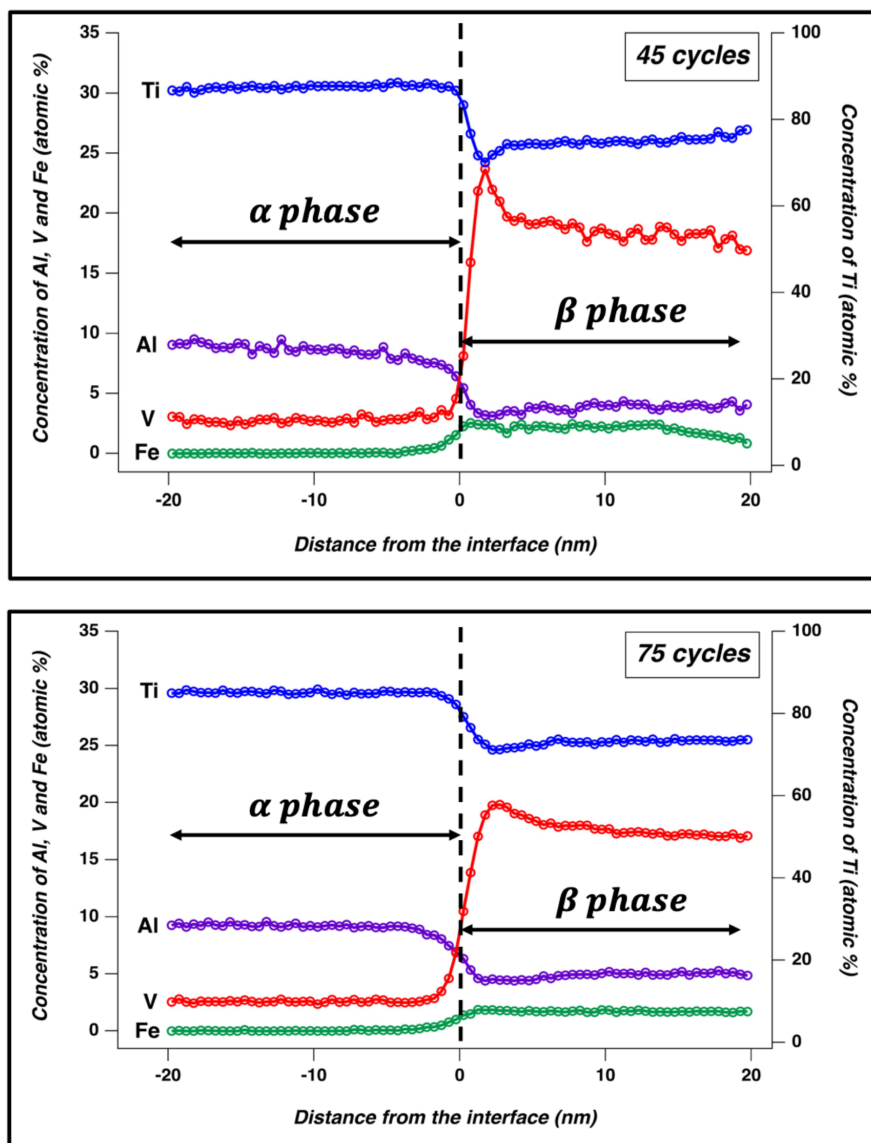


Figure 5.6: Proximate histogram of the 45cycles and 75cycles constructed from the reconstructed atom maps indicating the decreased Vanadium (17 – 18 at%) in the β phase.

the 0cycle sample was used to calculate the T-zero temperature using ThermoCalc software with TCTI2 database and was found to be 929.85 °C [141]. This confirms that displacive transformation of the α to β phase with this composition is not possible between 400 °C and 650 °C. However, these calculations assume that both α to β phases are in a pristine condition with no stored energy due to accumulated plastic strains from thermo-mechanical reversals as performed in our experiments.

5.3.2 *On Stored Energy due to cyclic plastic deformation*

The plastic strain accumulation within a phase can be estimated from the peak broadening effect by extracting the full width half max (FWHM) from the neutron diffraction peaks. FWHM values were calculated by single fit peak analysis using the VDRIVE program [136]. Figure 5.7 shows a plot of the the FWHM values (from both Bank1 and Bank2) of the $\alpha(101)$, $\alpha(100)$, $\alpha(002)$ and $\beta(110)$ peaks versus the thermo-mechanically cycled samples. It is clear that the FWHM values are higher than that of the 0Cycle sample, indicating an increase in the accumulation of plastic strain (i.e., dislocation density) in both phases. Interesting, a sharp increase in the FWHM of the β phase is noticed. This is indeed expected. In the Ti6Al4V system, the β phase is a minor phase (~ 2 to 5%) at lower temperatures. Nevertheless, due to its crystallographic structure being BCC, it is likely that the plastic strain partitions to the β phase initially. Once the β phase has fully strained to a limit, a shift of the plastic strain to the α phase occurs. As the thermo-mechanical reversals proceed, plastic strain continues to accumulate in the α phase. This result implies that during rapid thermo-mechanical gyrations, at some point there occurs a shift in the plastic strain partitioning from the β to the α phase, which in turn may lead to dynamics of “stored energy” in these two phases and may affect thermodynamic local equilibrium at interfaces between these phases.

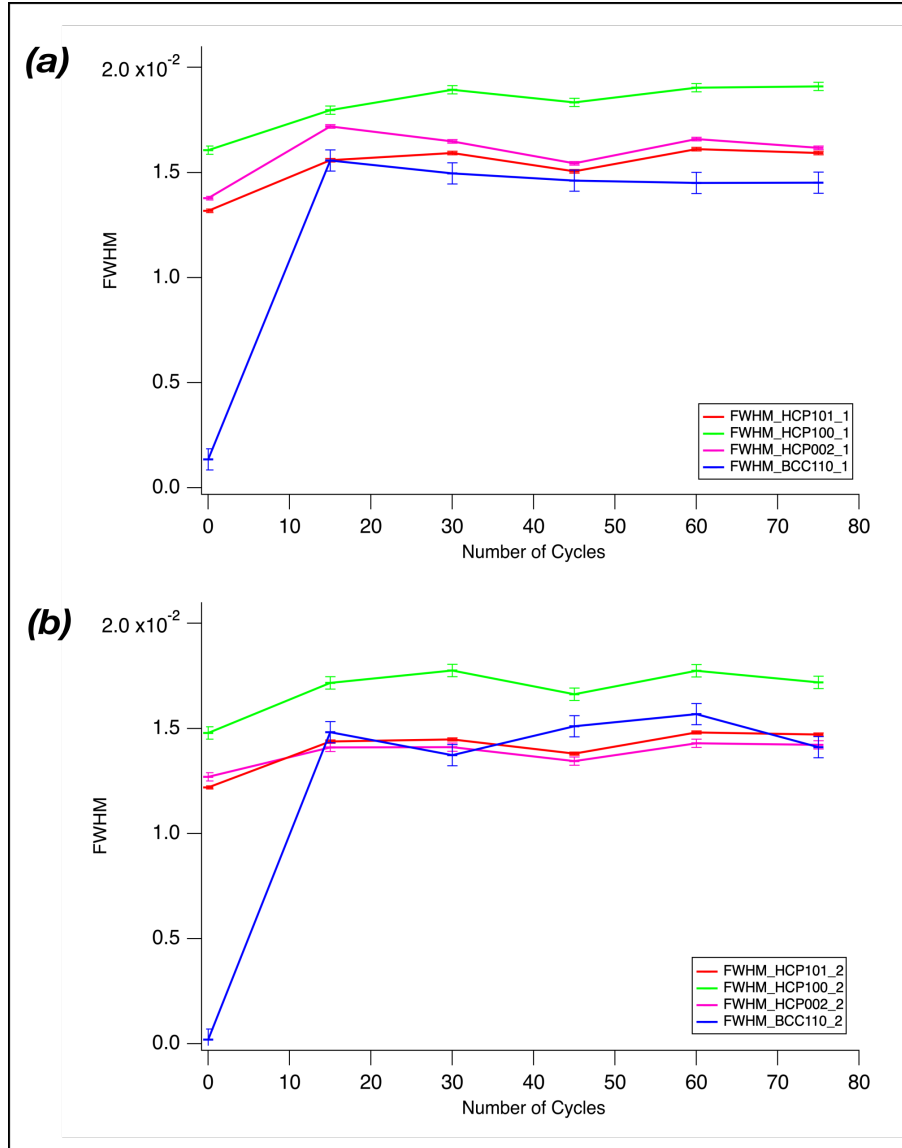


Figure 5.7: FWHM plots from Bank1 (top) and Bank2 (bottom).

5.3.3 *Dynamic Local Equilibrium at Interfaces*

If the stored energy within the β and α phases do have an effect on the local equilibrium at the interface, it should be reflected in the concentration of inter-phase boundaries. The excess energy stored in the α phase, relative to the β phase, could trigger a dynamic transformation [86]. To validate this theory, thermodynamic phase boundary calculations were done with ThermoCalc (TCTI2 database) [141]. Since Ti6Al4V is a multi-component system that has many other subsidiary phases, only the (HCP_A3) α phase and the (BCC_B2) β phase are considered in this analysis. An arbitrary amount of energy (in units of J/mole) is removed sequentially from the β phase, i.e., stabilizing the β phase with reference to the α phase, in the increments of 100J/mole at 650 °C ¹. The higher temperature limit of 650 °C was chosen because this is the upper temperature limit in our thermo-mechanical reversals and the atomic mobility may be higher to arrive at local thermodynamic equilibrium at α/β interfaces. With every increment of 100J/mole energy, the β phase boundary line shifts downwards (i.e., reduction of vanadium in β phase) as shown in Figure 5.8. The atom probe concentration profiles are then overlaid onto the calculated phase boundary lines.

The comparison confirms that vanadium at the α/β phase interface of the 45cycles samples, matches the $(\alpha + \beta)$ phase boundary line calculated with reduction of 400J/mole energy in β phase. Similarly, with the 75cycles sample, the vanadium concentration coincides with the phase boundary line calculated with a reduction of 500J/mole energy. In other words, an increase in stored energy of 400 to 500 J/mole in the α phase is expected to make it unstable, triggering a transformation to the β phase. These analyses give an insight on the role of localized and accumulated plastic strains that can shift the interface stability that is attained purely based thermal boundary conditions.

¹Note: The above calculations will yield the same results, if the energy is added to α phase instead of removing the energy from the β phase, because thermodynamic calculations are only sensitive to relative differences in the molar free energy of a given phase.

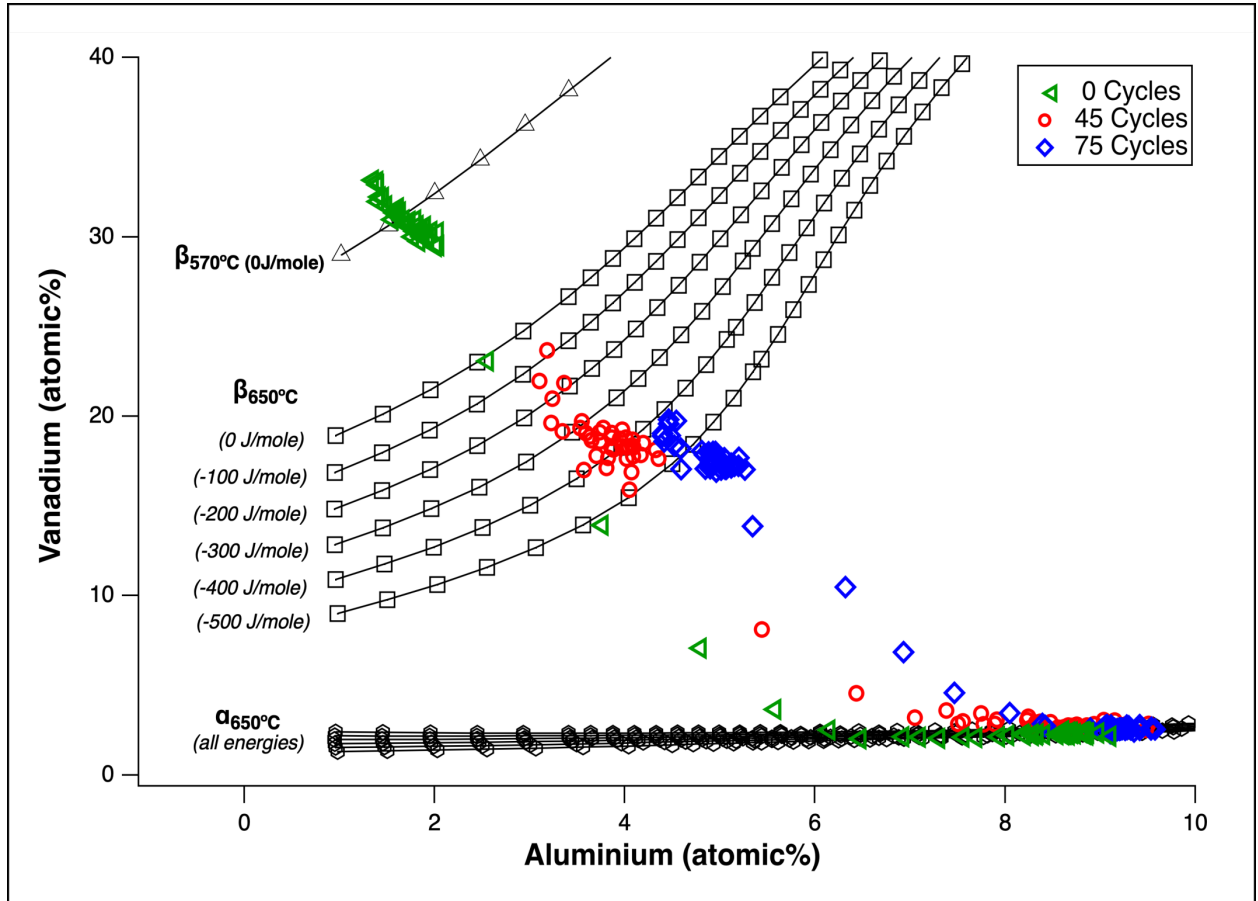


Figure 5.8: Downward shift of the equilibrium phase boundary lines of β , with every incremental reduction of 100J/mole from the molar free energy of the β phase. An overlay of the experimental data on to the phase boundary lines indicating that the concentration of the vanadium in the thermo-mechanically cycled samples (45cycles and 75cycles) matched the phase boundary line calculated with 400-500J/mole energy reduction in the β phase

5.3.4 *Role of accumulated plastic strains on interface mobility*

As mentioned earlier, the diffusivity of vanadium is low in the temperature range of 400 °C and 650 °C (10^{-18} to 10^{-16} m²/s), respectively. This may severely impact the interface mobility. Diffusion controlled growth calculations using DicTra[®] for a single thermal cycle showed that the interface velocity is nearly zero (approaching 10^{-12} m/s) and the local equilibrium concentration at the α/β phase interface on the β -side reached more than 60 at.% [141]. Therefore, we postulate that the observed redistribution of alloying elements and movement of β/α interface can only be rationalized based on invoking accelerated diffusion through dislocations and defects, also commonly known as pipe diffusion. Pipe diffusion plays a more dominant role at lower temperatures where the bulk diffusivity of alloying elements is generally restricted, which is the case in our alloy system [22, 152]. We hypothesize that the buildup of dislocations occurs in the α phase close to the β/α interface. This increased dislocation density at the interface allows for the diffusion of vanadium across the interface, allowing for the growth of the β phase into the α phase, depicted in Figure 5.9. Based on the above discussions and our measured solute concentration profiles across the α/β interface, we conclude that the reconstructive transformation pathway is more likely to occur during these dynamic thermo-mechanical gyrations involving plastic strains.

TEM analysis² across the gauge section of the 75cycles sample was done to study the dislocation substructures across the α and β phases. The operating hypothesis for the mechanism of the dynamic transformation of $\alpha \rightarrow \beta$ in AM Ti6Al4V, under TM cycling conditions is postulated to be based on enhanced diffusion of V through dislocation pipes. In evidence of this, bright field (BF) and weak beam dark field (WBDF) images from the ‘75cycles’ sample were obtained. As shown in Figure 5.10(a), complementary centered BF

²Collaborative work with researchers at The Ohio State University.

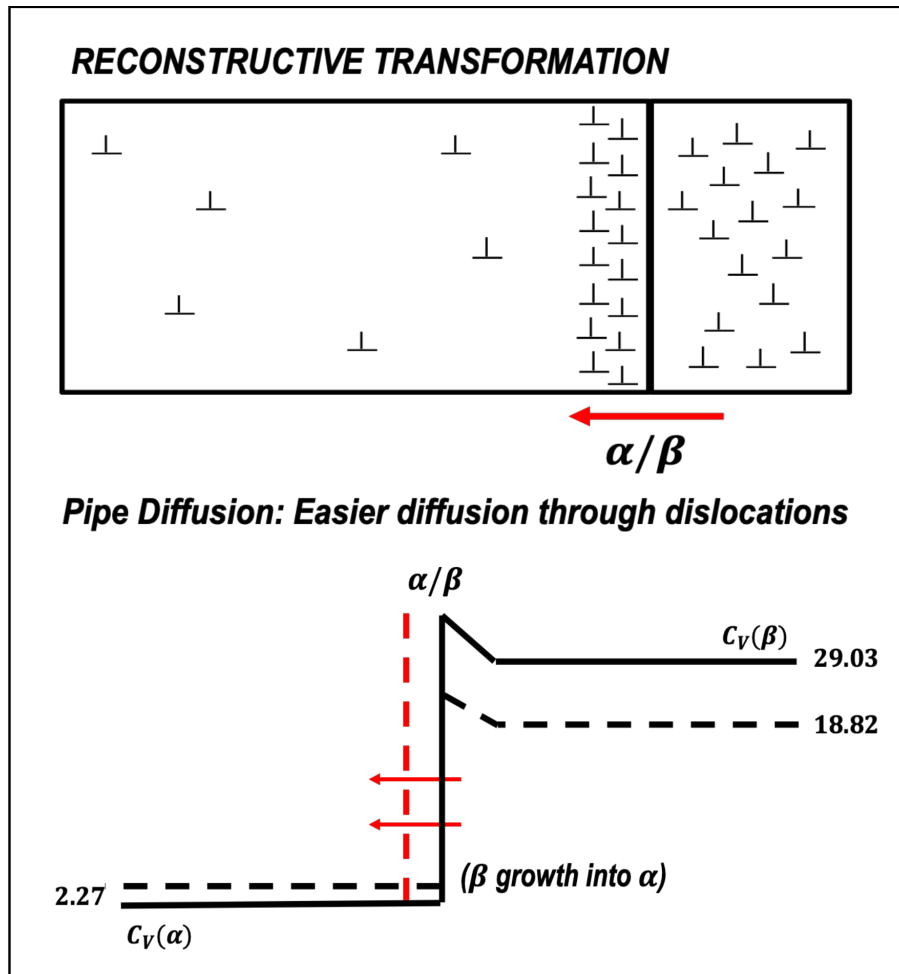


Figure 5.9: Schematic of the strain accumulation hypothesis.

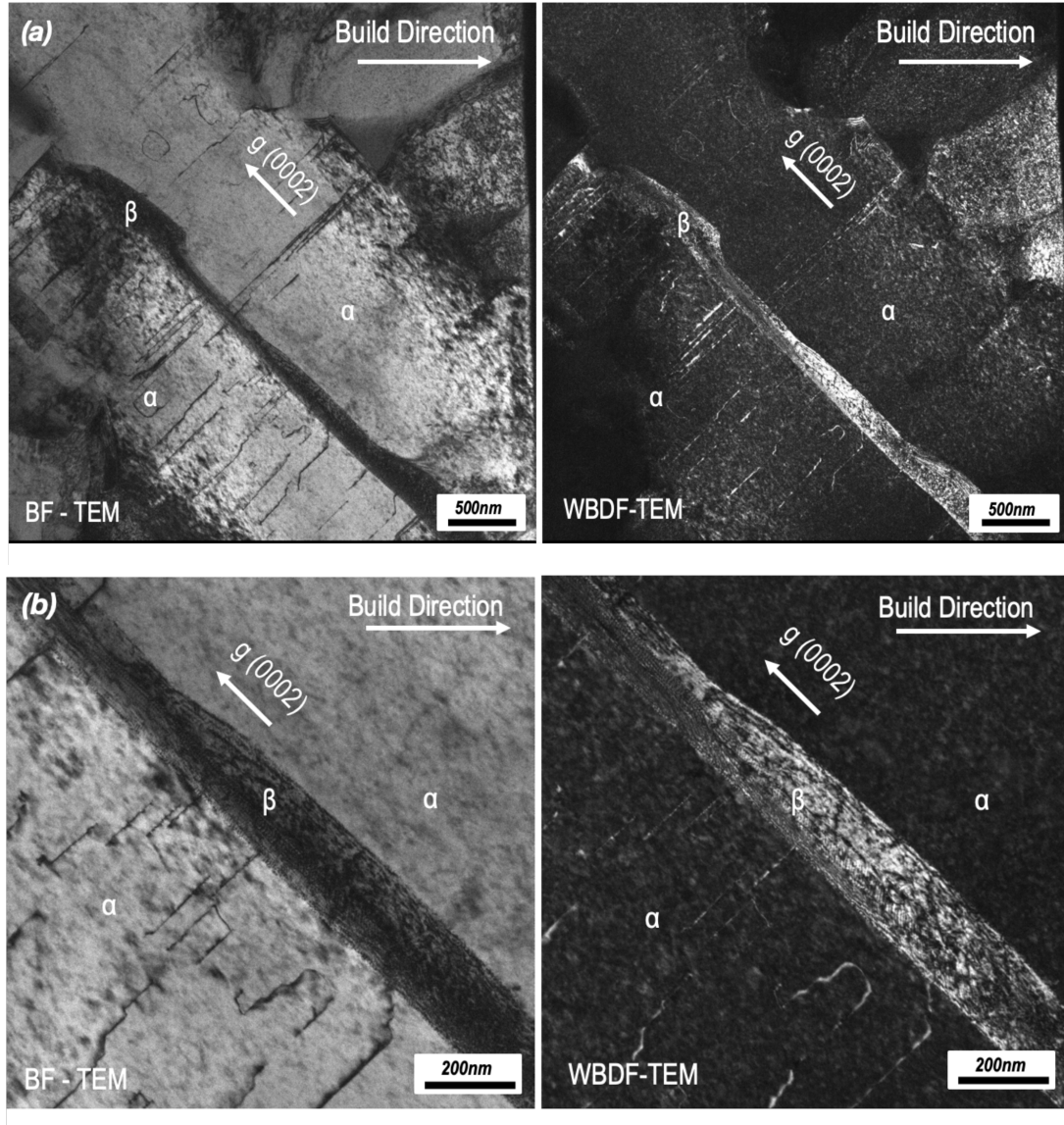


Figure 5.10: Complementary Bright Field and weak-beam Dark Field images of the α and β phases from the 75cycles samples. (a) Dislocation lines scattered across the bulk of the α lath emitting out of the α/β interface; (b) A magnified view of the β rib showing the presence of dislocations.

and WBDF images were obtained by orienting the α phase along the $\{0\bar{1}10\}$ zone axis and setting up a two-beam condition along (0002) basal reflection (Blackburn & Williams). The images revealed dislocation segments of the $\langle c+a \rangle$ type within the bulk of the α phase, with most dislocation segments originating at the α/β interface [73]. This emission of dislocations from the α/β interface, induced by the presence of the β plates in a Ti6Al4V system has been reported before by Castany et al. [74]. In addition, they have also confirmed that the β ribs do not inhibit the transmission of dislocation across α lamellar colonies [77]. When transmission of a dislocation occurs, residual dislocations are created at the α/β interface [76].

BF and WBDF images obtained at higher magnifications also revealed dislocations within the β phase as shown in Figure 5.10(b). The dark contrast within the bright β phase in the WBDF image indicates the presence of a combination of extrinsic dislocations, originating due to the thermo mechanical cycling across the 150nm β rib. Additionally, intrinsic misfit type dislocations along the α/β interface are also observed, as seen from the periodic striations adjacent to the β phase. These dislocation segments emitted from the interface will potentially act as conduits for V diffusion and thereby facilitate the $\alpha(\beta)$ transformation.

5.3.5 *Reevaluation of Displacive Transformation with stored energy*

Shape changes accompanying the $\alpha \rightarrow \beta$ transformation occurs by the rotation of the α grains [99]. In poly-crystalline materials, such as in our case, α grain rotations are restricted and hence deformation bands accommodate the plastic strains, and this phenomenon has been shown by Jourdan et al [153]. Their experimental work also indicates that when dislocations in the α phase are isolated within the matrix, they do not act as preferential nucleation sites for β to form. But when multiple dislocations interact with each other forming tangles and

sub-boundaries, they can act as potential nucleation sites for α to nucleate via a diffusion-less pathway [70, 153].

Since displacive transformation occurs by a coordinated movement of atoms that result in a structure change, the newly nucleated phase will inherit the composition of the parent phase. However, one could argue that our observed redistribution could be the result of two-step process, i.e., displacive transformation of α structure to β structure with no change in composition first and redistribution of vanadium in β phase in the second step. Previously, we estimated the T-zero temperature without stored energy to be 929.85 °C. With the new formulation based on the stabilization of β phase by reduction of 500 J/mole, the T-zero temperature was recalculated. The new T-zero temperature was found to be 774 °C which is still higher than 650 °C, thereby ruling out the possibility of displacive transformation in our experiments.

5.4 Summary of chapter

This chapter can be summarized as:

(1) Thermo-mechanical reversals were imposed on an AM Ti6Al4V alloy, with each sample subject to a specific number of TM reversals. The macro stress-strain response resulted in an overall softening as previously reported. Thus, the behavior of the softening remained consistent as a result of TM reversals. Neutron diffraction analysis indicated an increase in the β phase fraction in all the TM cycled samples.

(2) In order for the β phase to grow, partitioning of solute elements must have had to take place. Atom probe tomography showed that the Vanadium concentration reduced from an initial of 30 at.% to 18 at.% in the TM cycled samples. This in-turn straddled the results

from the neutron diffraction analysis which showed a doubling of the β phase fraction (2.5% in 0cycles to 5.7% in 45cycles) post thermo-mechanical reversals.

(3) Thermodynamic calculations were performed to evaluate the effects of accumulating plastic strains in the α and β phases. Calculations indicated that an estimated increase of 400 to 500 J/mole of stored energy in the α phase is necessary to trigger a $\alpha \rightarrow \beta$ phase transformation. Analysis from the solute concentration profile ruled out the hypothesis of a displacive type of transformation. Rather, in order to attain local equilibrium at the α/β interface, a possible reconstructive type of transformation is likely to have occurred. Additional TEM examination across the α/β interface indicated a highly dislocated β rib, with dislocations emitting out of the α/β interface into the α phase, proving our hypothesis of pipe diffusion.

CHAPTER 6

Temporal transients of strain partitioning between α and β phases in Ti6Al4V alloy during Thermo-Mechanical gyrations

In the previous chapters, ex-situ rapid thermo-mechanical gyrations revealed an increased β stability. A hypothesis of the strain partitioning between the α and β phases and the dynamic $\alpha \rightarrow \beta$ transformation was put forth based on the interface solute concentration profile. Although the ex-situ study indicated interesting phenomenon's during thermo-mechanical gyrations, a time-resolved development of strain partitioning and dynamic transformations will provide a better understanding of the influence of thermo-mechanical gyrations. Therefore, in this chapter, a temporal resolution of these events of strain partitioning during thermo-mechanical gyrations is studied with in-situ experiments using high energy X-ray diffraction at the FAST beamline at CHESS. Strain accumulation events are tracked with time at a temporal resolution of 0.5 seconds. A quantitative analysis of the partitioning of Al and V across the α/β interface is examined. The details in this chapter are currently being drafted as a manuscript for publication.

6.1 Experimental Setup

6.1.1 *Thermo-mechanical reversals at FAST Beamline, CHESS*

X-ray diffraction at FAST Beamline, CHESS:

In-situ thermo-mechanical reversals were conducted on an AM Ti6Al4V sample at the FAST beamline at Cornell High Energy Synchrotron Source (CHESS). The FAST beamline is equipped with a Rotation and Axial Motion (RAMS2) tensile/compressive load frame. The RAMS2 is a screw driven loadframe that allows for a 360° rotation without impeding the incoming X-ray beam as the sample is measured in-situ [154]. As shown in Figure 6.1, a monochromatic X-ray beam of 41.991keV ($\lambda = 0.295 \text{ \AA}$) energy with a dimension of 2mm x 2mm is directed onto the sample. Diffracted X-ray frames are collected on to GE detector placed at a distance of 867mm from the sample. This distance was optimized to measure atleast 3 β peaks for our analysis. The GE detector is a 40cm squared flat panel area detector having a 2048 x 2048 array of 200 μm pixels [155]. The detector distance and instrument parameters are the calibrated using a CeO₂ standard reference material. A constant flow of Argon was maintained around the sample during the experiment to provide an inert atmosphere to avoid oxidation or oxygen pick-up, because Ti6Al4V is known for its affinity to oxygen which stabilizes the α phase. Since our experiments call for in-situ measurements during complex thermo-mechanical cycling in addition to our specimens being highly textured (since they are AM fabricated), a fixed ω value is chosen for the entire run of the TM cycle. Sample rotations would hamper the temporal events of strain partitioning and therefore, TM reversals were done with a fixed ω value. This angle was chosen in order to get a strong β peak (usually at $\omega=90^\circ$ or $\omega=120^\circ$). A typical x-ray diffraction ring

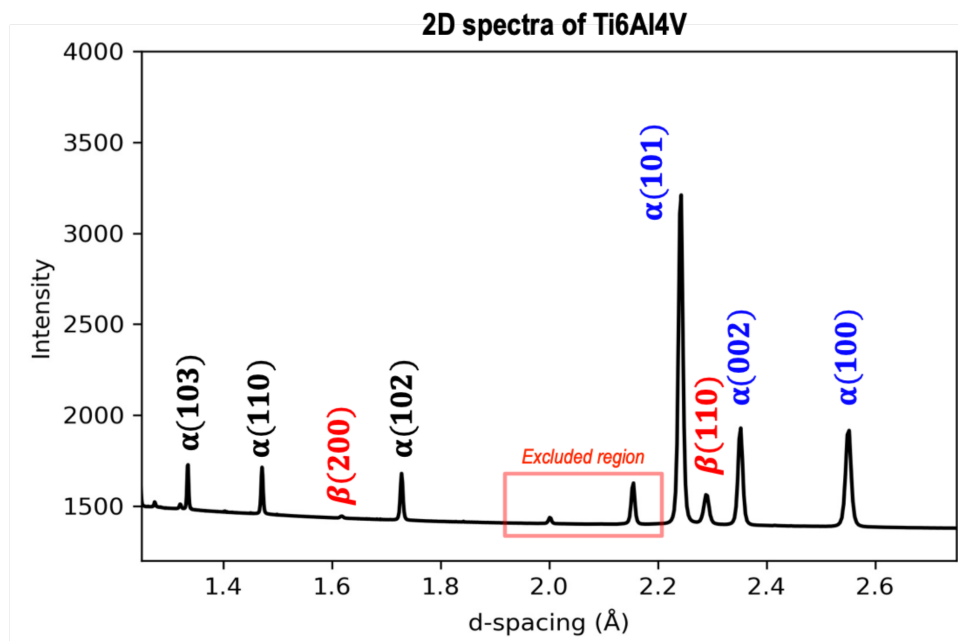
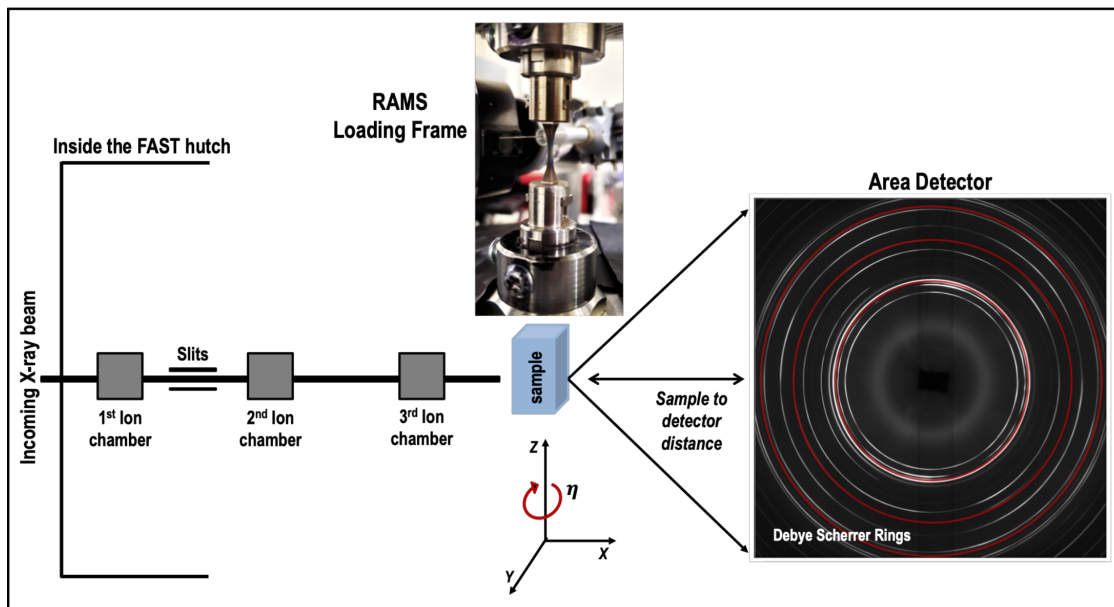


Figure 6.1: (Top) Experimental setup at the FAST beamline, CHESS with a picture of the sample mounted on the RAMS2 load frame. X-ray diffraction ring pattern on the GE detector with the rings highlighted in red corresponding to the β phase; (Bottom) Intensity versus d-spacing plot indicating the α and β peaks.

pattern collected on the GE detector is shown in [Figure 6.1](#), where the rings marked in red are of the β phase. X-ray images frames were collected at a frame rate of 0.5 sec/frame.

Data analysis and strain calculation:

Integration and conversion of the Debye-Scherrer rings into 2D Intensity versus d-spacing plots was done with Reitveld refinements using GSAS-II software [156]. For our analysis, 2D diffraction plots were generated by the integration of the diffraction rings over the entire 360° azimuth range, as shown in [Figure 6.1](#). 2θ values were converted to d-spacing with the fixed wavelength of $0.295 \text{ \AA}$. The d-spacing spectrum in our analysis ranges from $1 \text{ \AA}$ to $2.7 \text{ \AA}$, which covered 9 α peaks and 3 β peaks. In our analysis, our focus will be on the 3 primary peaks of α , $\alpha(100)$, $\alpha(002)$ and $\alpha(101)$ and 2 β peaks, $\beta(110)$ and $\beta(200)$. The intensity of the third β peak was too small to refine and add in our quantitative analysis of the phase. Two unknown peaks due to detector contamination, marked by a box region, were excluded from our analysis. The unknown peaks are likely a residual on the GE detector or noise from the thermocouples, and the exclusion of these peaks does not affect our analysis in anyway. Lattice strains in the individual hkl planes of the two phases were calculated by [Equation 4.1](#) [4.1.2](#). Single peak fitting with GSAS-II was used to extract FWHM values during TM cycling from the $\alpha(100)$, $\alpha(002)$, $\alpha(101)$, $\beta(110)$ and $\beta(200)$ peaks. Since AM samples are highly textured in the as-fabricated stage, the spherical harmonic preferred orientation option was included to compensate for the inherent texture component in both phases.

Thermo-mechanical experimental set-up:

Thermo-mechanical reversals were imposed on an AM Ti6Al4V sample on a RAMS2 load frame. The complex setup of the experiments did not allow for the use of the DIC system for strain control experiment and hence, strain control was achieved by moving the screw head to a defined position, i.e. displacement control. Constant-displacement TM reversals were conducted, where the screw head was set to move a $\pm 0.10 \text{ mm}$ displacement in compression

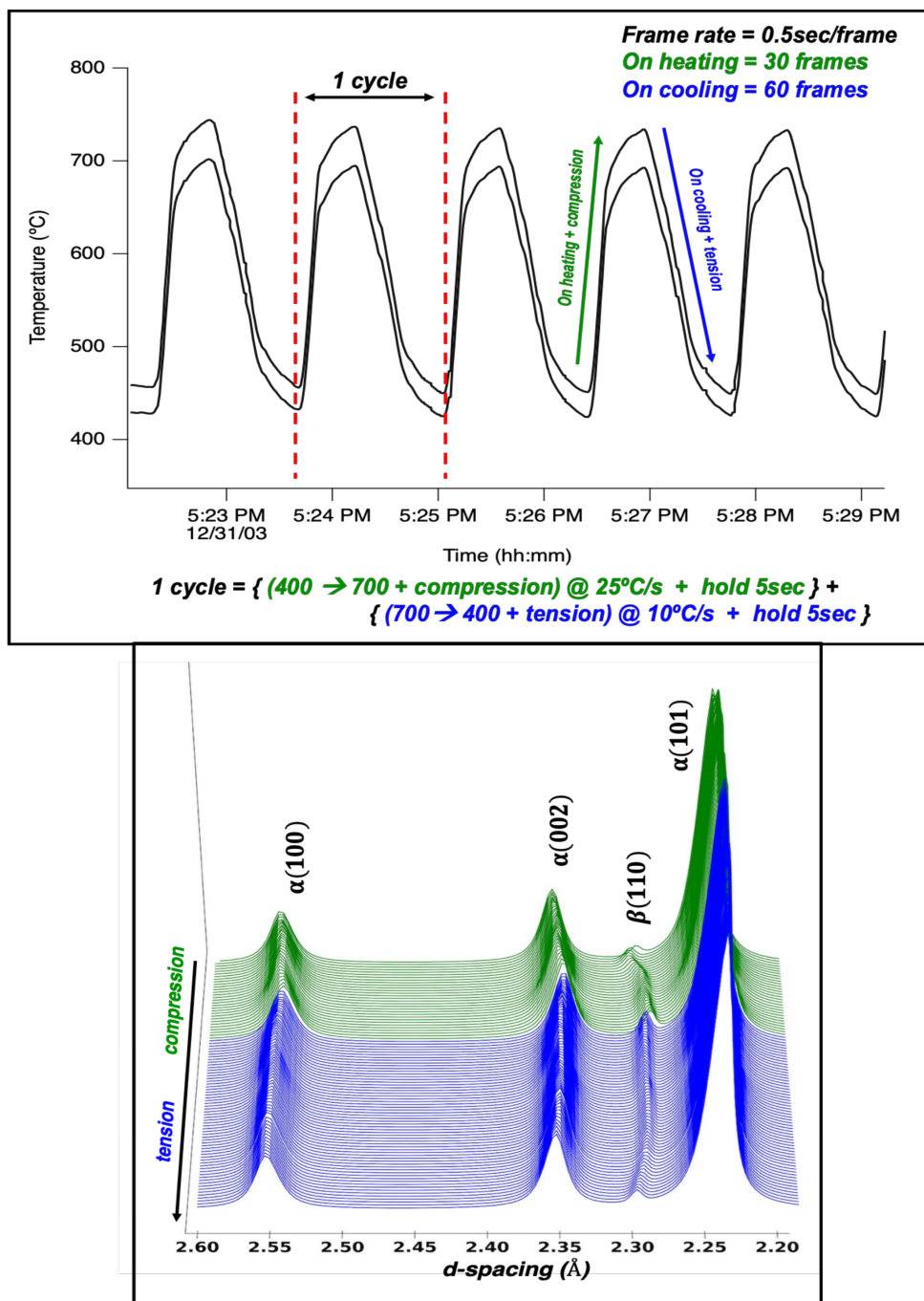


Figure 6.2: Description of the Thermo-mechanical cycle; (Bottom) 90 Intensity versus d-spacing plots plotted in sequence of one thermo-mechanical cycle (compression + tension)

and tension. Samples were prepared according to beamline specifications, with a gauge area of 1mm x 1mm. A typical thermo-mechanical cycle is shown in [Figure 6.2](#). Temperature control was maintained by placing thermocouples in the vicinity of the gauge section of the sample. As in our previous TM cycles, fast heating ($400^{\circ}\text{C} \rightarrow 700^{\circ}\text{C}$ at 25°C/s) and slow cooling rates ($700^{\circ}\text{C} \rightarrow 400^{\circ}\text{C}$ at 10°C/s) were maintained. On heating, a compressive load is applied (by movement of the screw head from an initial position of 0.15 to 0.05 mm). This is followed by a hold of 5 seconds and then cooling takes place with a simultaneous tensile load (screw head position is first unloaded to initial position of 0.15 and then moved to 0.25mm). Each TM reversal experiment consisted of 25cycles in total. Thus, with a frame rate of 0.5 second/frame, 1 TM cycle consisted of 90 frames. In total, each TM experiment dataset consists of an analysis of 2000 frames. In this chapter, our analysis will focus on 2 samples - (1) TM cycled sample and a (2) thermally cycled sample.

6.1.2 *Atom Probe Tomography*

In order to take a closer look at the concentration profiles at the α/β interface, nano-scale Atom probe Tomography was done on the thermo-mechanically cycled samples at Northwestern University, Evanston in collaboration with Dr. Dieter Ishiem. FIB coupons were selectively picked out from the gauge section of the TM sample as this was the prime region of focus. Atom probe needles were prepared with the FEI Helios system and sharpened to a tip radius of $\sim 30\text{-}40\text{nm}$. Atom Probe Tomography was performed on the LEAP 5000XS equipment with a laser wavelength of 355nm at a base temperature of 30K. A pulse energy of 19pJ was maintained throughout the experiment at which the $\text{Al}^+/\text{Al}^{++}$ mass peak ratio remained at 8. Each dataset consists of 100M+ ions for a good statistical analysis following which the 3D visualization and quantitative analysis of the data was done with IVAS 3.6 software. Proximity histogram (Proxigram) analysis was done across the α/β interface at 10

at% Vanadium. 1D concentration profile were also measured across the β phase to extract information on the composition gradient in the β phase.

6.2 Results of the in-situ Thermo-mechanical reversals

The in-situ thermo-mechanical reversals studied in this chapter vary from the previous in-situ neutron diffraction experiments detailed in [chapter 4](#) in terms of the temporal resolution ($\sim 300\text{sec}/\text{cycle} + 1\text{hour}$ hold periods for data collection) of the events that occur in Ti6Al4V during thermo-mechanical reversals. In this study, high energy X-rays of $0.295\text{\AA}$ wavelength penetrate through the cross section ($1\text{mm} \times 1\text{mm}$ gauge area) of the sample and diffract onto an area detector. A time-resolved evolution of plastic strains, with a temporal resolution of $0.5\text{sec}/\text{frame}$, within each individual $\{hkl\}$ plane of the α and β phases are examined with precise registration of macro scale temperature and stress gradients.

6.2.1 *Macro Stress-Strain response*

The macroscopic mechanical response shown in [Figure 6.3](#) comprises of the displacement(mm), Stress (MPa) and temperature($^{\circ}\text{C}$) versus time. The load response is converted to stress with a known sample gauge area of ($1\text{mm} \times 1\text{mm}$) and is shown in [Figure 6.3\(b\)](#). As seen from the stress-time plot, an asymmetry in the stress is noticed, where on tension, an increase in the stress during TM reversals is observed. Initially, stress on the tensile side (measured at 400°C) starts at $\sim 620\text{MPa}$ and gradually increases to $\sim 730\text{MPa}$ during TM cycling. Whereas on the compressive side (measured at 700°C), a decrease in the stress is noticed from an initial of $\sim 410\text{MPa}$ to $\sim 370\text{MPa}$ at the end of cycling. This asymmetry in the stress levels can be rationalized by the temperature-mechanical dependent property of metal alloy systems. Since, our TM reversals are displacement control in addition to

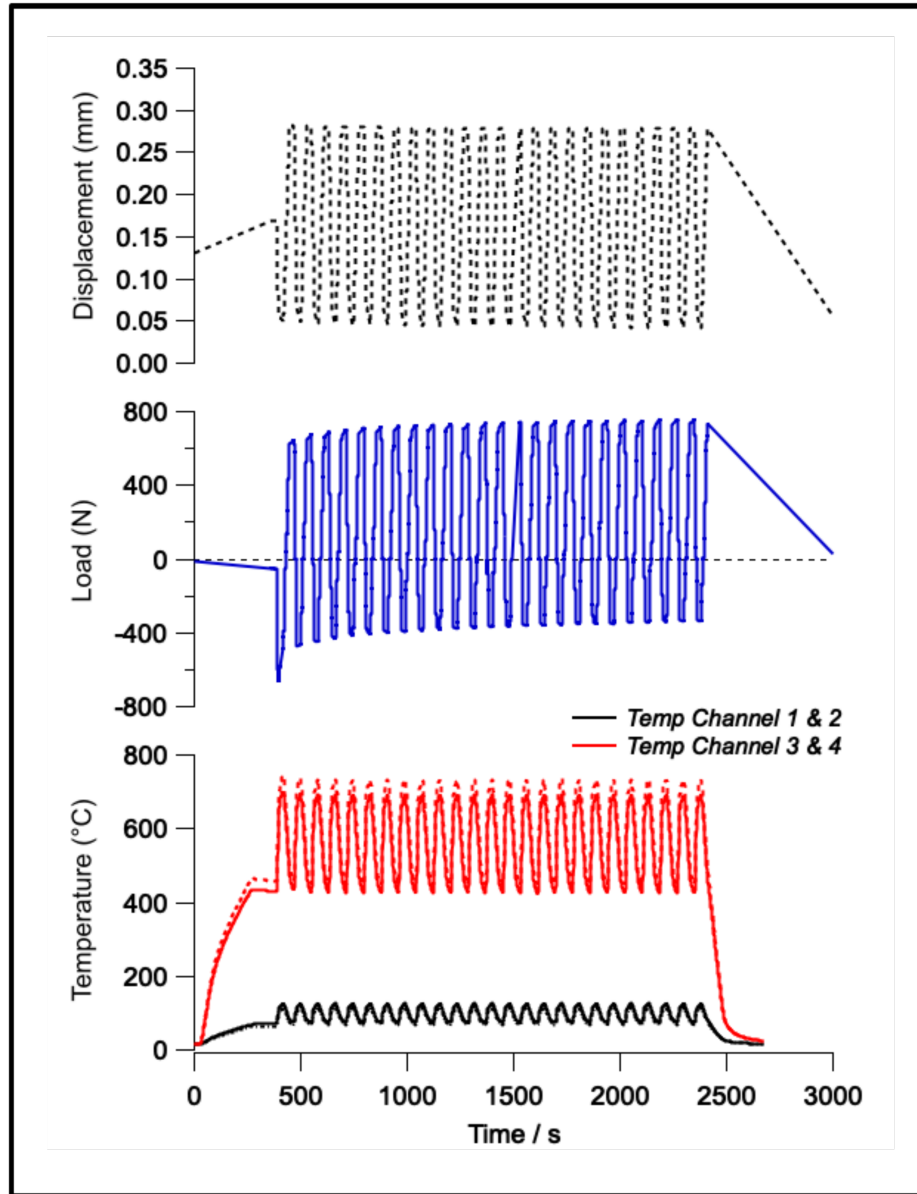


Figure 6.3: Macro stress-strain response - Displacement, Stress and Temperature versus time graphs.

temperature fluctuations, an uneven strain is applied on tension (at 400 °C) and compression (at 700 °C), resulting in this asymmetric behavior. The macro-mechanical stress response from the current in-situ experiments differs from our previous ex-situ strain-controlled TM reversals, where the macro stress-strain response observed a gradual softening trend, on compression and tension, during TM reversals. Nonetheless, plastic strains are imparted to the sample. By occurring so, the micro-mechanical response of the α and β can now be tracked and analyzed.

6.2.2 *Elastic strain evolution in α and β phases*

To comprehend the dynamics of elastic strain partitioning between the α and β phases during thermo-mechanical reversals, lattice strains within each $\{hkl\}$ plane was calculated by the changes in the d-spacing values as per equation [Equation 4.1](#). The initial d_o values for each peak $\{hkl\}$ is measured from the sample at room temperature before TM cycling. The initial lattice constants of the α phase measured to be $a=2.925 \text{ \AA}$ and $c=4.67 \text{ \AA}$, and likewise in the β phase measured at $a=3.20 \text{ \AA}$.

Lattice strains calculated here are a summation of the thermal+mechanical effects during cycling. Shown in [Figure 6.4](#) is the tracking of the evolution of lattice strains of the 3 primary α peaks, i.e., the prismatic planes $\alpha(100)$, the basal planes $\alpha(002)$ and the pyramidal planes $\alpha(101)$. The overall increase in the elastic strains as seen by the evolution of elastic strains straddle the overall macroscopic stress during thermo-mechanical reversals. The effect TM reversals on lattice strains is largely pronounced in the basal $\alpha(002)$ planes when compared to the pyramidal $\alpha(101)$ planes and prismatic $\alpha(100)$ planes. The lattice strain evolution is also tracked in the β phase, with the $\beta(110)$ and the $\beta(200)$ peaks is shown in [Figure 6.5](#). Interestingly the lattice strains as seen in the $\beta(110)$ peak, shows an initial minor increase

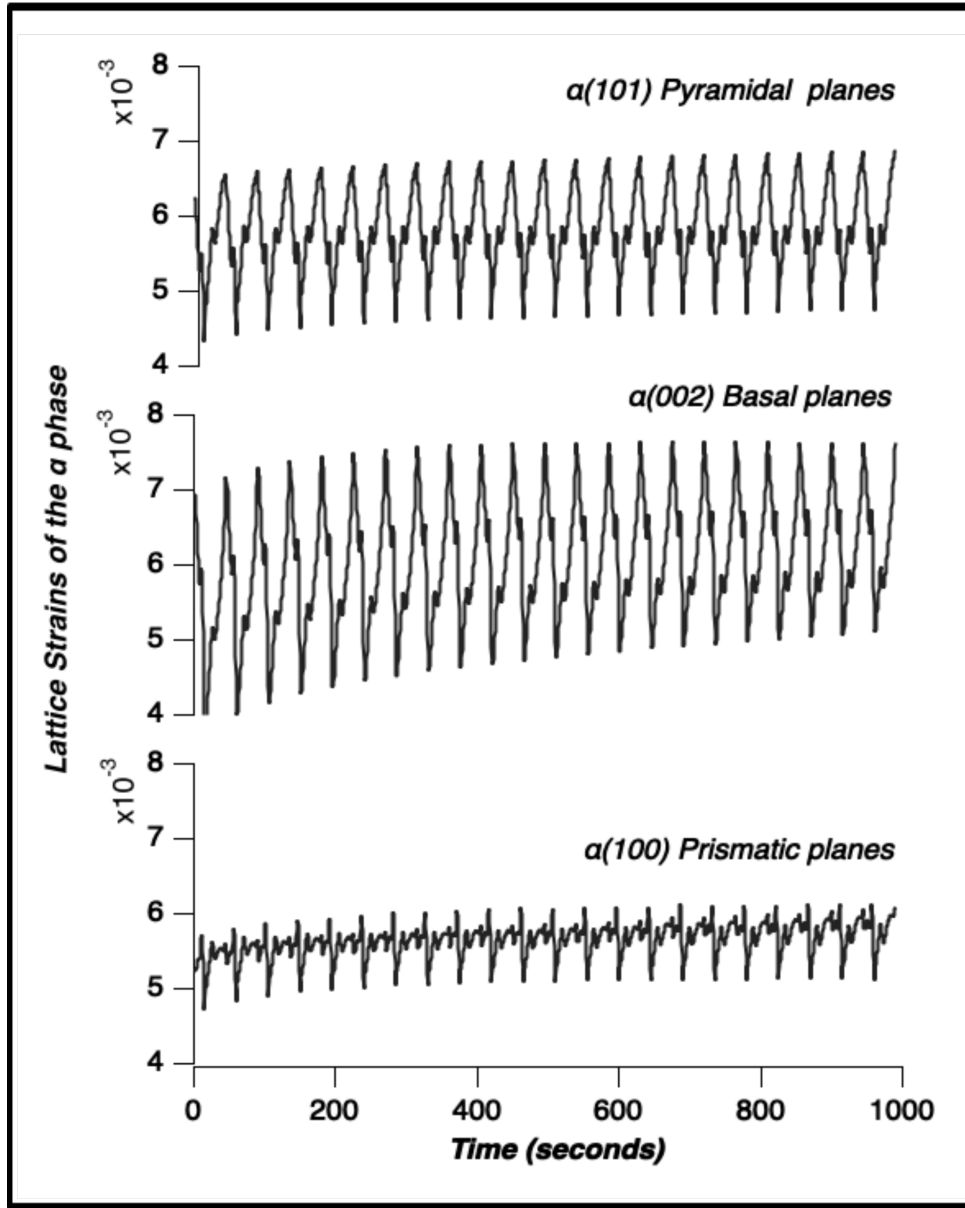


Figure 6.4: Lattice strains of the α phase tracked from the $\alpha(100)$, $\alpha(002)$ and $\alpha(101)$ peaks.

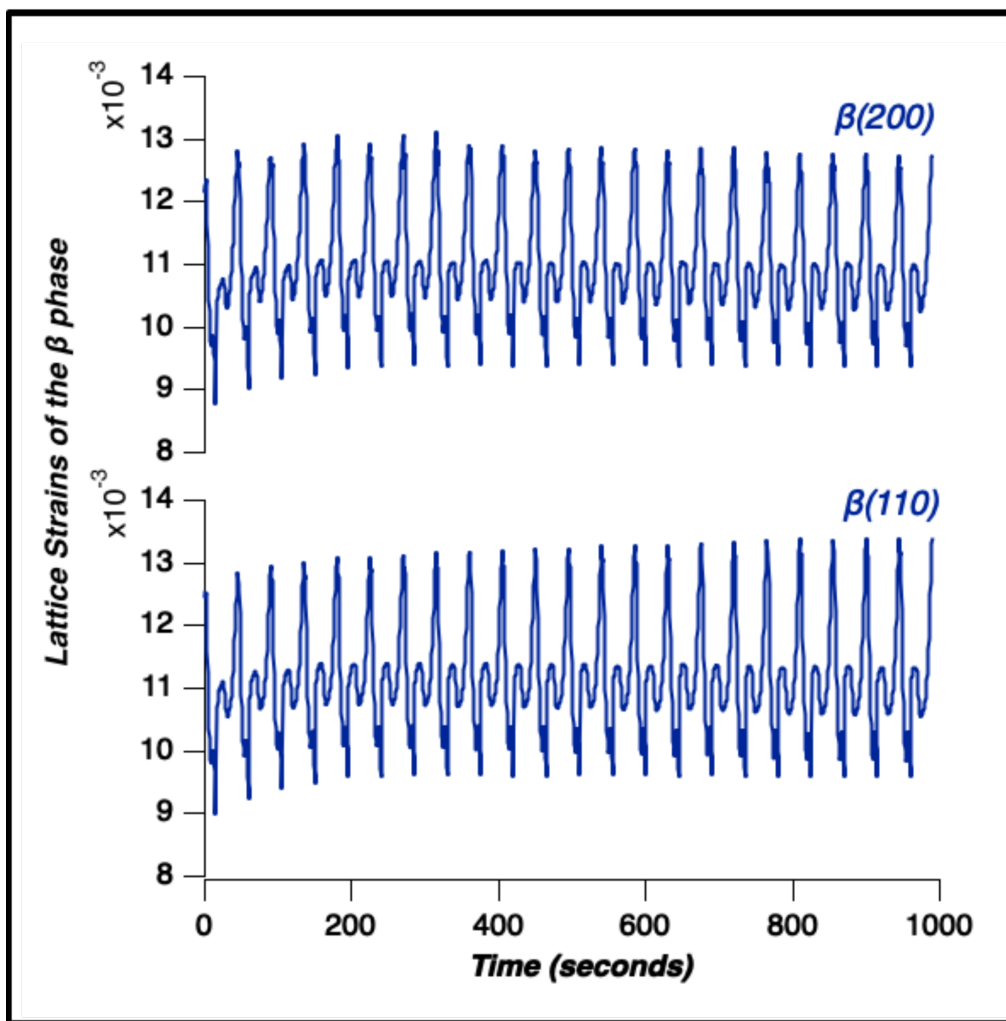


Figure 6.5: Lattice strains of the β phase tracked from the $\beta(110)$ and $\beta(200)$.

in the first 5-7 cycles, after which there seems to be a negligible effect as further thermo-mechanical reversals are imposed.

Phase fraction analysis of the samples before and after cycling was done to analyze the potential dynamic transformations that occurred during thermo-mechanical reversals. Phase fractions were measured from the thermo-mechanically cycled sample before and after being subject to TM reversals at room temperature. Initial phase fraction values in the α and β phase measured to be $97.2 \pm 0.01\%$ and $2.8 \pm 0.01\%$ respectively. The overall residual impact of the thermo-mechanical reversals was measured from the TM cycled sample (at room temperature) post TM cycling revealed that the phase fraction of β increased to $3.5 \pm 0.01\%$ as noticed with a sharper $\beta(110)$ peak along with an increase in the lattice parameter of $a=3.22 \text{ \AA}$. These results straddle the previously reported dynamic phase transformation kinetics during TM reversals from the ex-situ TM cycles experiments.

6.2.3 *The impact of thermal fluctuations*

The thermo-mechanical reversals conducted thus far are a complex combination of thermal and mechanical signatures. To deconvolute the thermal component and study the effect of thermal cycles on the α and β phases, one of the samples is subjected to thermal fluctuations between 400°C and 650°C (with similar thermal rates maintained for the thermo-mechanical runs). Shown in [Figure 6.6](#), are the lattice expansion and contraction events of 3 cycles, seen in the $\alpha(101)$, $\alpha(002)$, $\alpha(100)$ and $\beta(110)$ peaks, and the calculated lattice strains, as a function of time.

Lattice strains were calculated for the individual $\{hkl\}$ planes and shown in [Figure 6.6](#). As the sample is thermally cycled, on heating a expansion of the lattice strain is noticed, and on cooling, the reverse effect of lattice contraction is noticed in all peaks. As expected, no accumulating effect of these elastic strains is seen as in the thermo-mechanical cycles

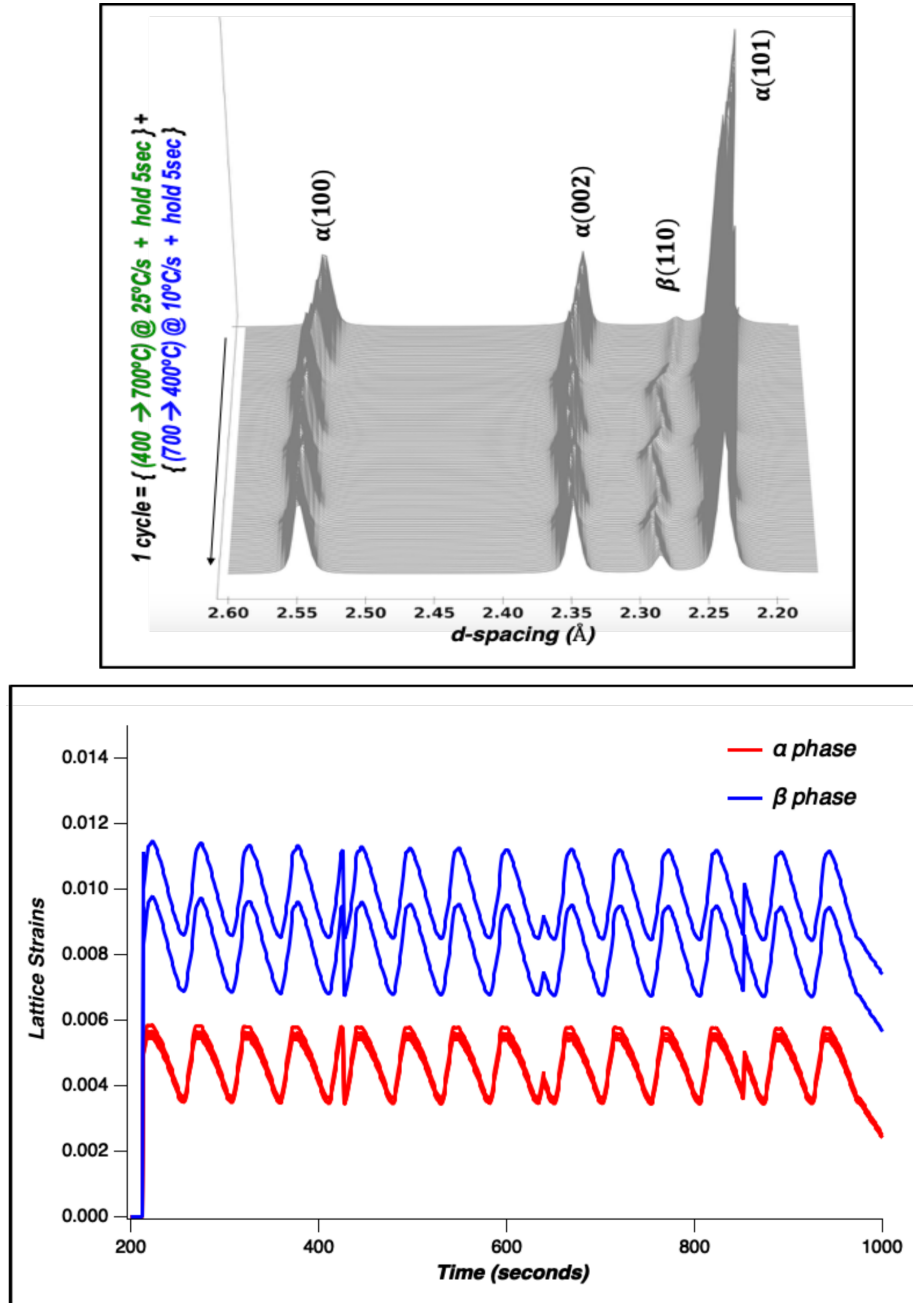


Figure 6.6: (Top) Evolution of d-spacing tracked in 3 thermal cycles showing expansion and contraction of the peak with time; (Bottom) Lattice strains of the α and β phases showing no changes in lattice strains.

sample. The changes in the lattice strains noticed is only an effect of the thermal expansion of the crystal lattice as it is cycled back and forth between 400 °C and 700 °C. This result indicates that thermal fluctuations have no particular impact on the α and β phases, since the temperature bounds of the thermal cycle is well within the $\alpha+\beta$ region, where long range diffusion of solute elements is too slow to trigger a phase transformation [157]. As can be seen from Figure 6.6, thermal strains of the α phase are at 0.006 at 700 °C and 0.0038 at 400 °C. The calculated thermal strain at 400 °C and 700 °C with a thermal expansion coefficient of $\alpha_{(\alpha-phase)}=9.7 \times 10^{-6}/^{\circ}\text{C}$ are $\epsilon_{700^{\circ}\text{C}} = 0.00689$ and $\epsilon_{400^{\circ}\text{C}} = 0.00388$. Similar trends are noticed in the β phase. The thermal strains calculated from the thermally cycled sample is well within the lattice strains calculated for the thermo-mechanically cycled samples.

6.2.4 *Evolution of lattice parameters of the α and β phase*

To evaluate the dynamic phase transformations of $\alpha \rightarrow \beta$ that occur as a result of thermo-mechanical reversals, sequential refinements was conducted on the 2000 frames of data from the TM cycled sample. But since the $\beta(200)$ peak is a peak with a relatively low intensity, a precise refinement of the peak during the sequential refinements proved challenging, and thus interpreting the phase fractions from this data seemed void. Thus, one way to look at phase transformation is to analyze the lattice constants of the α and β phases during reversals. Lattice parameters of the α phase ($a(\text{\AA})$ and $c(\text{\AA})$) and β ($a(\text{\AA})$) phases were calculated based on the relative 2θ positions of the diffraction peaks and is shown in Figure 6.7. The lattice parameters of the HCP phase tracked during TM reversals, show a minor increase in the a and c parameters as shown in Figure 6.7(a). The high c/a ratio (1.596 - 1.599), as shown in Figure 6.7(b), is associated with a lamellar ($\alpha+\beta$) microstructure [158]. Kaschel et al. showed that an increase in the c/a represents a phase transformation of the crystal lattice [159]. Now looking at the β phase, Elmer et al. have shown that changes in lattice constant

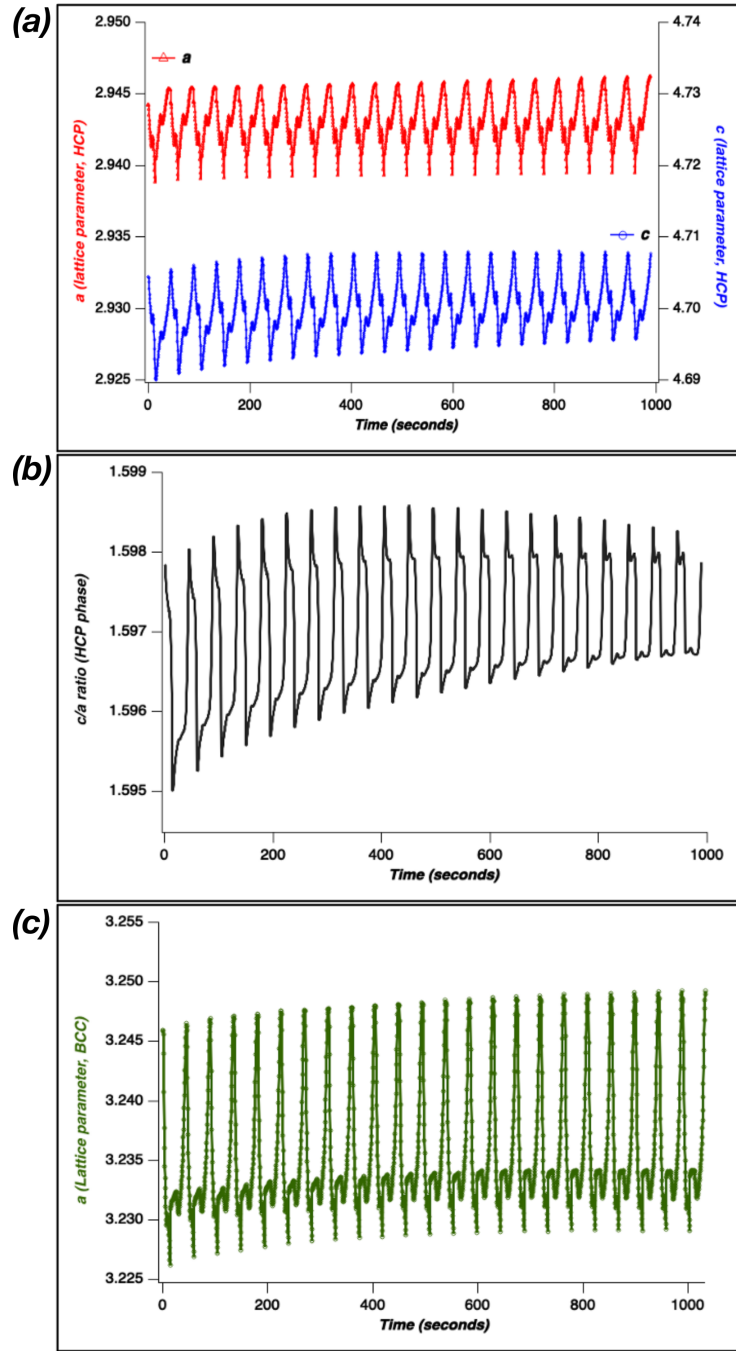


Figure 6.7: Evolution of the (Top) α lattice constants (a and c); (Mid) c/a ratio of the α ; (Bottom) β lattice constant (a), with time.

of the β phase is caused due to a phase transformation which involves the partitioning of Vanadium to the β phase [157]. During the $\alpha \rightarrow \beta$ transformation, Vanadium is spread in a increasing volume of the β phase, which would lead to a decrease in the Vanadium concentration in the β phase. The decreased Vanadium is accompanied by an increase in the lattice parameter of the β phase. Figure 6.7(c), shows an increasing trend of the lattice parameter of the BCC β phase. The above changes in the lattice constants in both phases indicate that a dynamic phase transformation is more likely to have occurred during out thermo-mechanical reversals.

6.2.5 *Solute concentrations across the α/β interface*

Phase transformations occur by the partitioning of AL and V across the two phases. Thus, to confirm the dynamic phase transformations of the $\alpha \rightarrow \beta$ and get a quantitative analysis across the interface, nano-scale Atom Probe tomography was conducted on the thermo-mechanically cycled sample. An uncycled sample is also looked at for a state of reference. Shown in Figure 6.8 is the 3D reconstructed atom map of the TM cycled sample. The reconstructed dataset of 350nm x 120nm consists of a β rib of 30-40 nm across the tip. The atom maps indicate a clear distinction in the partitioning of solute elements across the interface, where the Al and O (TiO ions) partition to the α phase. Whereas V and Fe show strong partitioning to the β phase. Iso-concentration surfaces at 10at.% Vanadium were constructed for a proxigram profile across the interface for both the reference sample and the thermo-mechanically cycled sample and is shown in Figure 6.9. The proxigram profile across the top interface measured an Aluminum concentration of 8.32 ± 0.18 at% and a Vanadium concentration of 2.62 ± 0.11 at% in the α phase. The β phase measured 2.3 ± 0.10 at% Aluminum and 25.1 ± 0.19 at% vanadium. These values correspond to the reported literature values of Al and V partitioning across the α/β interface in EBM Ti6Al4V.

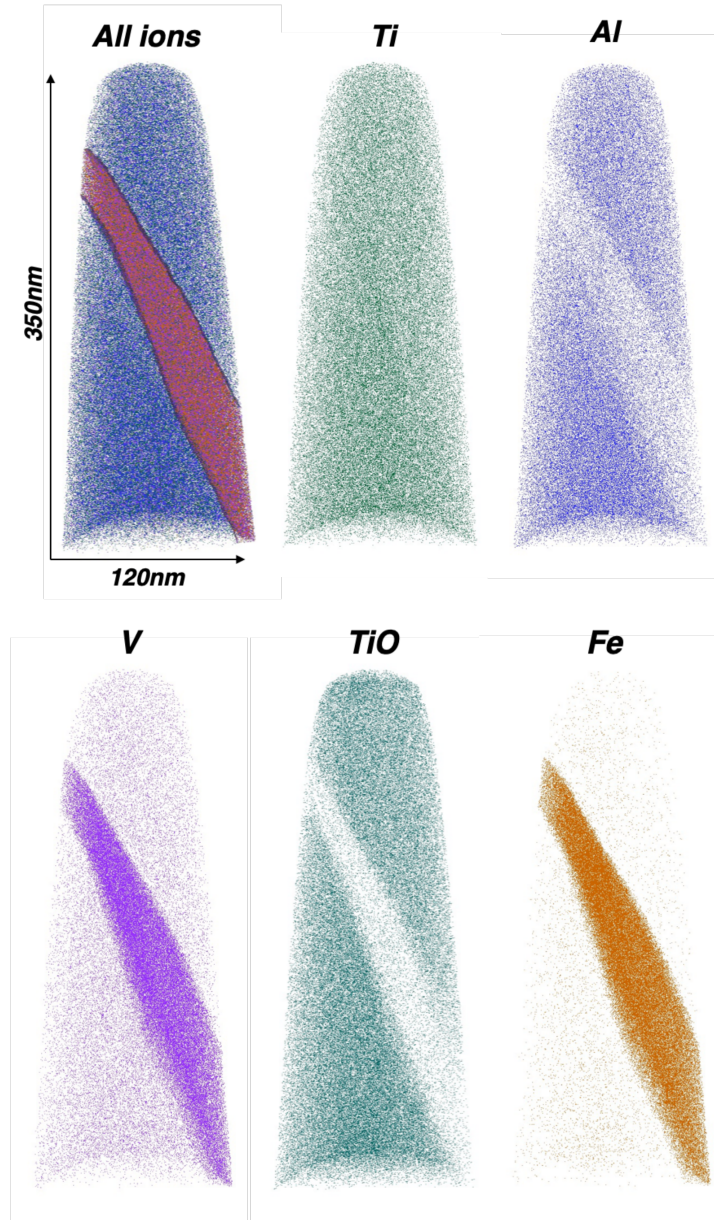


Figure 6.8: 3D reconstructed atom maps of the thermo-mechanically cycled sample showing the Ti, V, Al, Fe and O partitioning in the α and β phases.

Oxygen is extracted from the TiO^+ and TiO^{++} molecular ions at 32Da and 64Da. The oxygen concentration in α is measured to be at 0.646 ± 0.05 at% and 0.19 ± 0.02 at% in the β phase. Concentrations of solute elements in the α and β phases are tabulated in [Table 6.1](#).

Proxigram analysis across 20nm of the α/β interface on either side of the interface was performed and is shown in [Figure 6.9](#). The analysis of the TM cycles sample measure a Vanadium concentration of 22.4 ± 0.19 at% in the β phase with negligible changes in the α phase. Slight changes are also noticed in the Titanium concentrations across the two phases. The partitioning of Vanadium, although not as large as previously measured from our ex-situ analysis on the 45cycles and 75cycles sample in [5](#), still indicates that solute redistribution occurred locally at the interface during thermo-mechanical reversals, i.e., a dynamic phase transformation from $\alpha \rightarrow \beta$. The minor, but significant change, in the Vanadium partitioning can be reasoned out to be a consequence of the reduced number of TM reversals (25cycles in our case, compared to the 45cycles in the ex-situ analysis [5](#)). Nonetheless, the changes in the Vanadium profile along with the changes in the lattice parameters further indicates that dynamic transformations did take occur.

A 1D concentration profile with a 25nm long cylinder, as shown in [Figure 6.10](#) focusing on the Vanadium and Aluminum concentration profile, is done to estimate a composition gradient across the β lath. A "bump" at the α/β interface on either side of the β rib can be seen. This has been previously reported to occur because of the low diffusivity of Vanadium at low temperatures.

<i>Phase</i>	<i>Alloying Elements</i>	<i>Reference sample (at.%)</i>	<i>TM cycled sample (at.%)</i>
<i>α Phase</i>	<i>Ti</i>	87.62 ± 0.16	87.41 ± 0.14
	<i>Al</i>	8.88 ± 0.14	8.69 ± 0.12
	<i>V</i>	2.46 ± 0.07	2.95 ± 0.06
	<i>Fe</i>	0.03 ± 0.01	0.03 ± 0.01
	<i>O</i>	0.53 ± 0.04	0.64 ± 0.03
<i>β Phase</i>	<i>Ti</i>	69.16 ± 0.2	70.61 ± 0.16
	<i>Al</i>	2.98 ± 0.08	3.38 ± 0.06
	<i>V</i>	25.45 ± 0.2	22.09 ± 0.15
	<i>Fe</i>	1.98 ± 0.06	1.78 ± 0.04
	<i>O</i>	0.09 ± 0.01	0.07 ± 0.01

Table 6.1: Concentration of the solute elements across the α and β phases across the reference sample and the thermo-mechanically cycled samples.

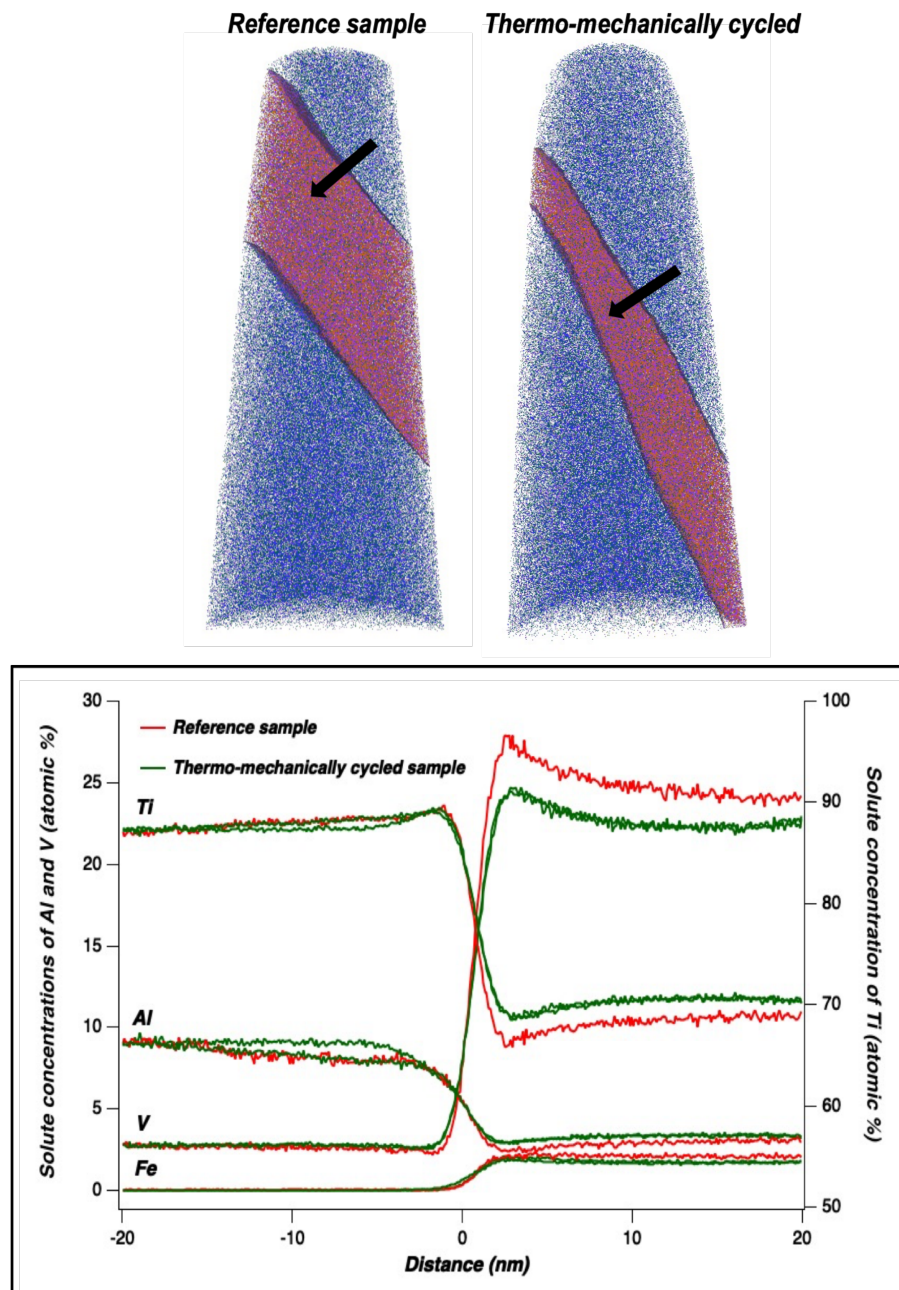


Figure 6.9: Proxigram analysis across the α and β phases in the reference sample and the TM cycled sample, showing a decrease in the Vanadium concentration of the TM cycled sample.

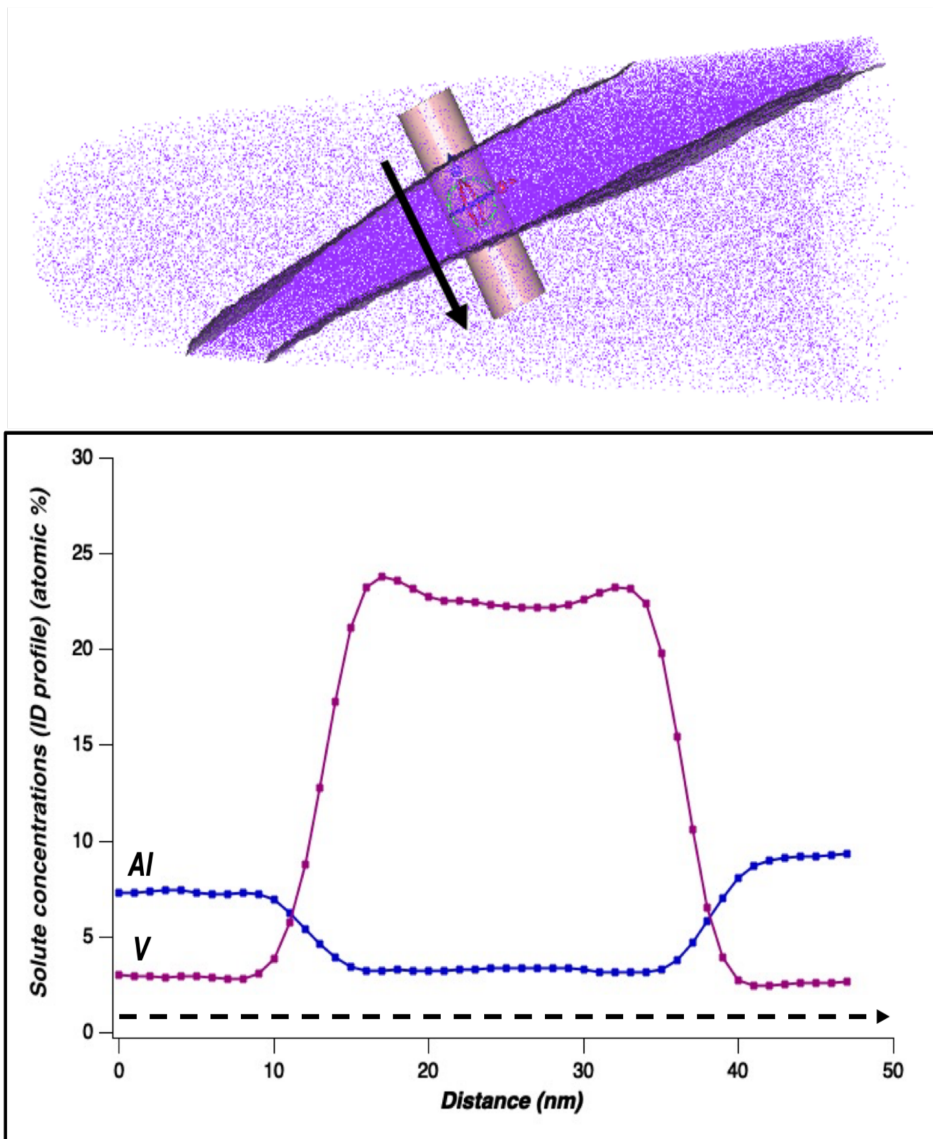


Figure 6.10: A 1D concentration profile (cylinder) across the beta rib in the TM cycles sample.

6.3 Discussion

The above results reveal the interesting temporal events of accumulating elastic/plastic strains and their preferential partitioning between the α and β phases during thermo-mechanical reversals between 400 °C and 700 °C. In addition, the analysis of the concentrations of Al and V across the α/β interface revealed a reduced Vanadium concentration in the β phase of the TM cycled sample. These results are discussed below in detail with theories from reported literature and validated with computational thermodynamics diffusion model.

6.3.1 Evolution of Lattice strains as a function of orientation

: Axial and Transverse strains are extracted from the diffraction image by integrating the ring over a 20° azimuthal range about the axial direction and the transverse direction as shown in [Figure 6.11](#). Analysis was done primarily focusing on the α phase. As seen from the lattice strain in the $\alpha(002)$ peak, as the axial strains show as increasing trend, whereas a consequent decrease in the transverse strains is noticed. Similar but subtle trends are also noticed in the $\alpha(100)$ and $\alpha(101)$ peaks. Shown in [Figure 6.12](#) is a closer look and correlation of the macroscopic stress to the are the axial and transverse lattice strains of the first TM cycle and last TM cycle [160].

The expansion and contraction of the crystal lattice as a result of heating and cooling during thermal cycling (Sec.6.2.3) is seen in [Figure 6.6](#). To further confirm the effect of the expansion and contraction we see in the individual lattice planes, elastic strains were measured across the axial and transverse directions (as shown in [Figure 6.11](#)). As expected, isotropic expansion and contraction effects of the lattice in the axial and transverse direction is noticed, indicating thermal effects. And thus, since this experiment was just a

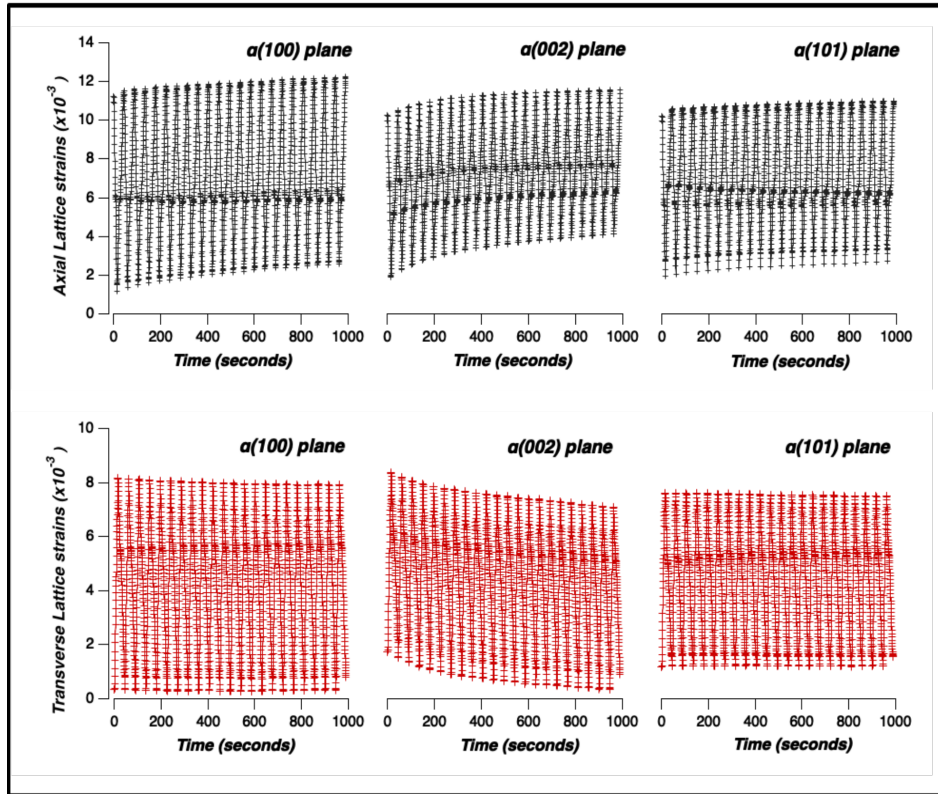
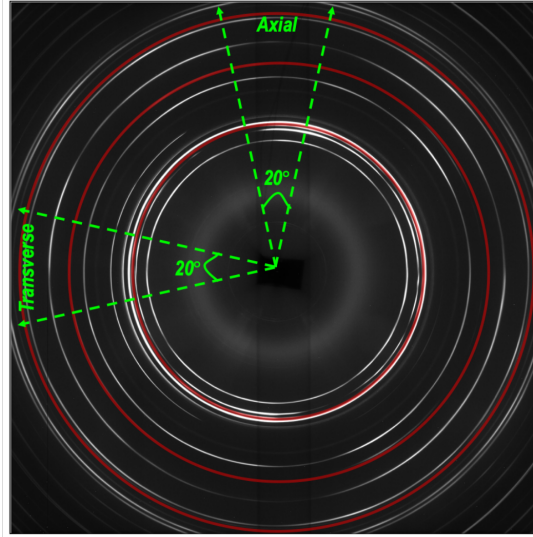


Figure 6.11: Elastic strains as a function of orientation - Transverse and Axial lattice strains in the α phase during thermo-mechanical reversals.

fluctuation in thermal cycling, the strain component measured here is a measure of the thermal strain (from the $\alpha(101)$, $\alpha(002)$ and $\alpha(101)$ peaks), where the $\epsilon_{thermal@650^\circ\text{C}} = 0.006$ and $\epsilon_{thermal@400^\circ\text{C}} = 0.0038$ is noticed in the α phase. This measured thermal strains in the α phase agrees well with the published thermal expansion co-efficient values for the α phase (in Ti6Al4V system) of $9.7 \times 10^{-6}/^\circ\text{C}$ [157].

6.3.2 *Plastic strain accumulation in α and β phases*

The accumulation of plastic strains within a phase can be interpreted from the peak broadening effects by analyzing the full-width-at-half-max (FWHM) values of individual peaks. Although, there are many contributions to the broadening of the peak, in our case temperature effects and complex strain reversals, in general, FWHM can be interpreted as the consequence of accumulating plastic strains, i.e., increase in micro-strain due to dislocations/defects and crystallite size effects. In our TM reversal cycles, not only did a peak shift occur (as seen from our lattice strain calculations), but an increase in the peak width is also noticed, as shown in Figure 6.13 and Figure 6.14.

For our analysis, the 3 primary peaks of α - $\alpha(100)$, $\alpha(002)$ and $\alpha(101)$ and the first two peaks of β , $\beta(110)$ and $\beta(200)$ are examined. FWHM is calculated by a single peak fitting with GSAS-II for each of the α and β peaks.

First, notice the trend of the FWHM in the β phase from the $\beta(110)$ and $\beta(200)$ peaks, shown in Figure 6.14. Our hypothesis of strain partitioning between the α and β phases rests on the fact that the BCC β phase has a greater number of active slip systems than the HCP α phase, will readily plastically strain during thermo-mechanical reversals. Once saturated with defects, plastic strains then shift to the α phase and start accumulating as further TM reversals are imposed. Evidence of a highly dislocated β phase is seen in 5.3.4.

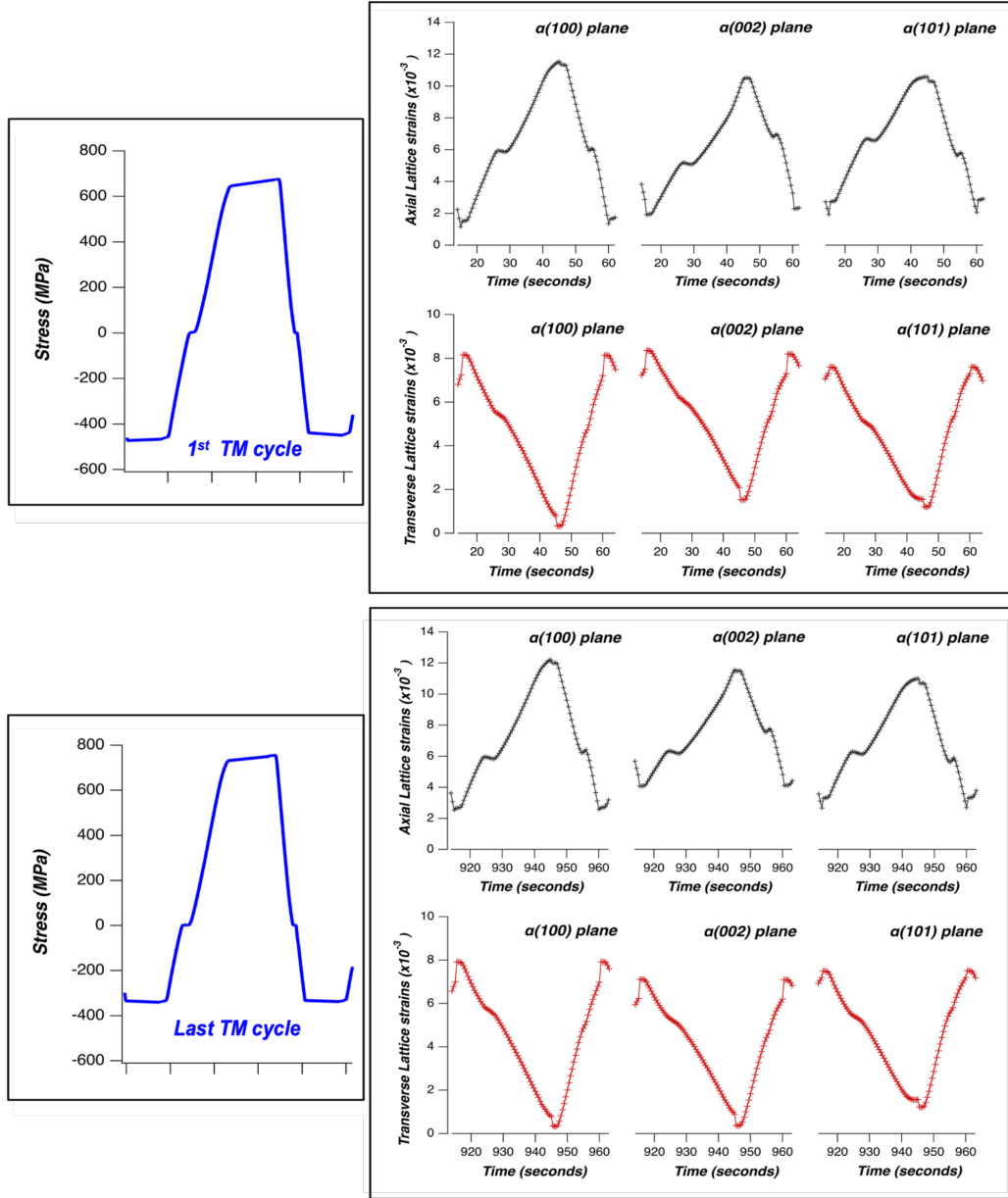


Figure 6.12: Axial and Transverse lattice strains of the α phase from the first cycle and the last cycle of the thermo-mechanically cycled sample.

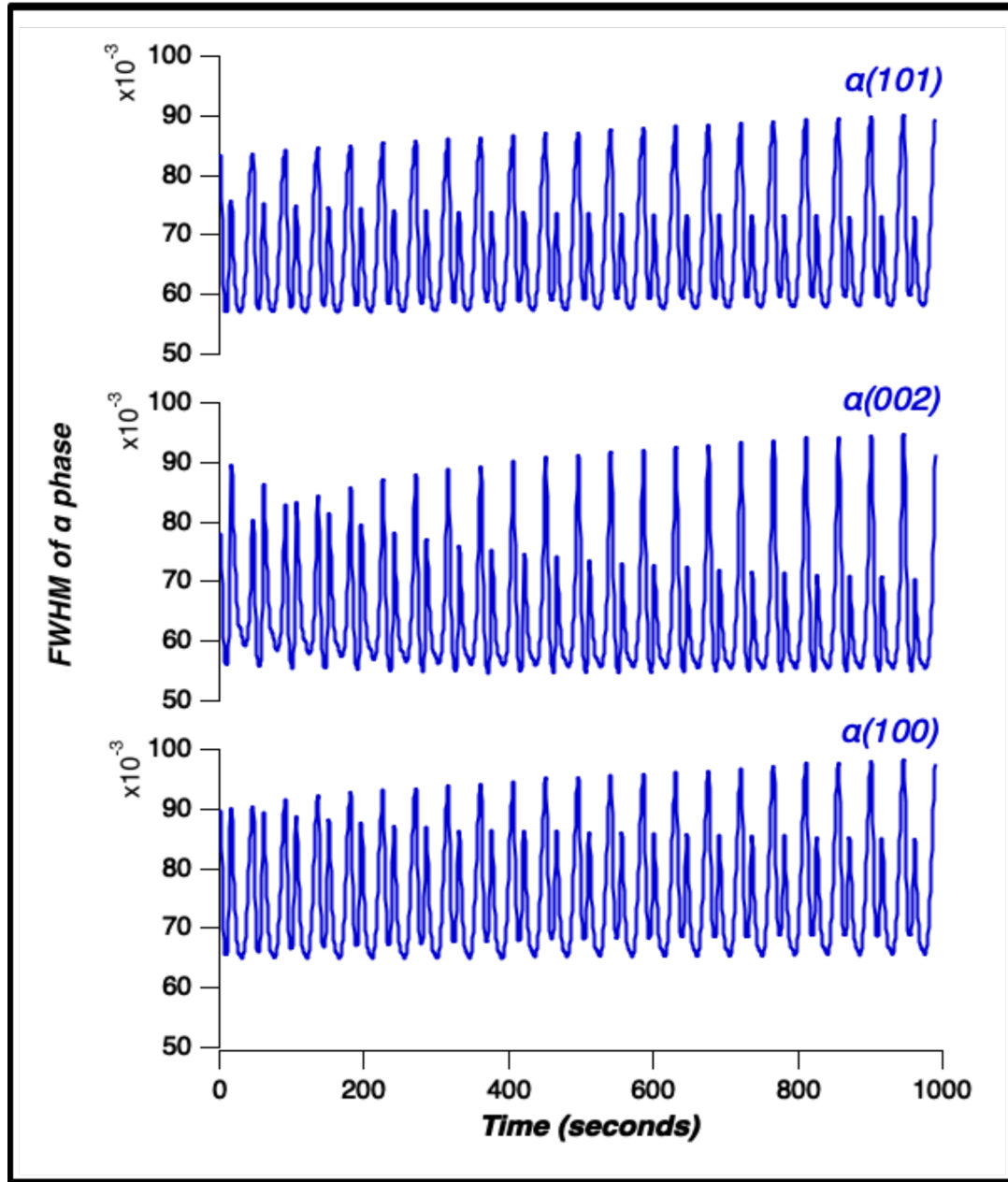


Figure 6.13: FWHM analysis (thermo-mechanically cycled sample) of the α phase showing the gradual strain accumulation in the $\alpha(002)$, $\alpha(100)$ and $\alpha(101)$ planes during TM cycling.

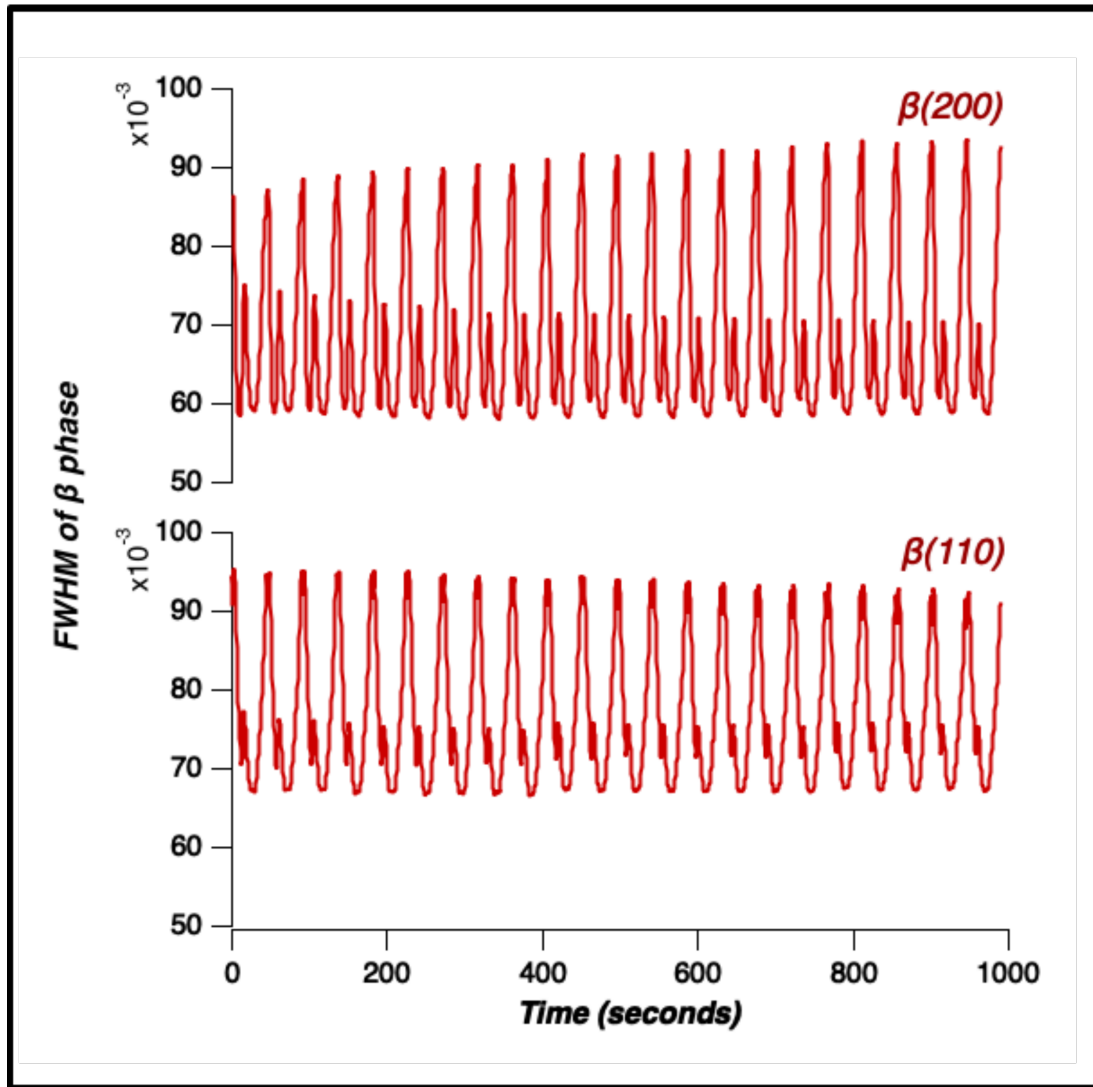


Figure 6.14: FWHM analysis (thermo-mechanically cycled sample) of the β phase showing no change, indicating a highly dislocated β .

Now looking at the trend in the FWHM from the $\beta(110)$ peak, the FWHM values remain near-constant throughout the TM reversals, thus indicative of a heavily dislocated β .

Secondly, the increasing effect of the FWHM is noticed in all the 3 α peaks during TM cycling shown in [Figure 6.13](#). Attributing the peak broadening effects because of strain broadening, plastic strain accumulation occurs in the α phase during TM reversals, i.e., an increase in the dislocation density within the α phase. The 3 most competing slip system in Ti alloy are the $\langle a \rangle$ Basal system, $\langle a \rangle$ Prismatic system and the $\langle a+c \rangle$ Pyramidal system [161]. A closer look at the 3 α peaks, show that the strain accumulation effects is highest in the basal $\alpha(002)$ planes. Although, both the prismatic $\alpha(100)$ and pyramidal $\alpha(101)$ planes show an increasing trend of the FWHM. This preferential trend in the strain partitioning among the α slip planes agree well with reported literature on the slip in the Ti systems. Bridlier et al. showed the co-existence of basal, prismatic, and pyramidal slip modes in Ti6Al4V and showed that the critical resolved shear stresses of the $CRSS_{Basal} < CRSS_{Prismatic} < CRSS_{Pyramidal}$ slip systems [77]. From our FWHM analysis, we do notice the activation of all 3 slip modes in addition to the basal planes having a higher impact on strain accumulation. The β phase taking in the plastic strains initially before accumulation partitions to the α phase. Although, further analysis of these plastic transients during thermo-mechanical reversals are yet to be analyzed, it is interesting to follow the overall strain accumulation events occurring in the α and β phase.

6.3.3 *Thermodynamic homogenization evaluation*

The above Atom Probe analysis indicated that a redistribution of solute concentrations occurred in the TM cycled sample, where the Vanadium concentration reduced from an initial of ~ 26 at% to ~ 22 at%. This reduction in the Vanadium solute concentration straddles the findings of the partitioning of solute elements as seen from our ex-situ analysis of the 45 and

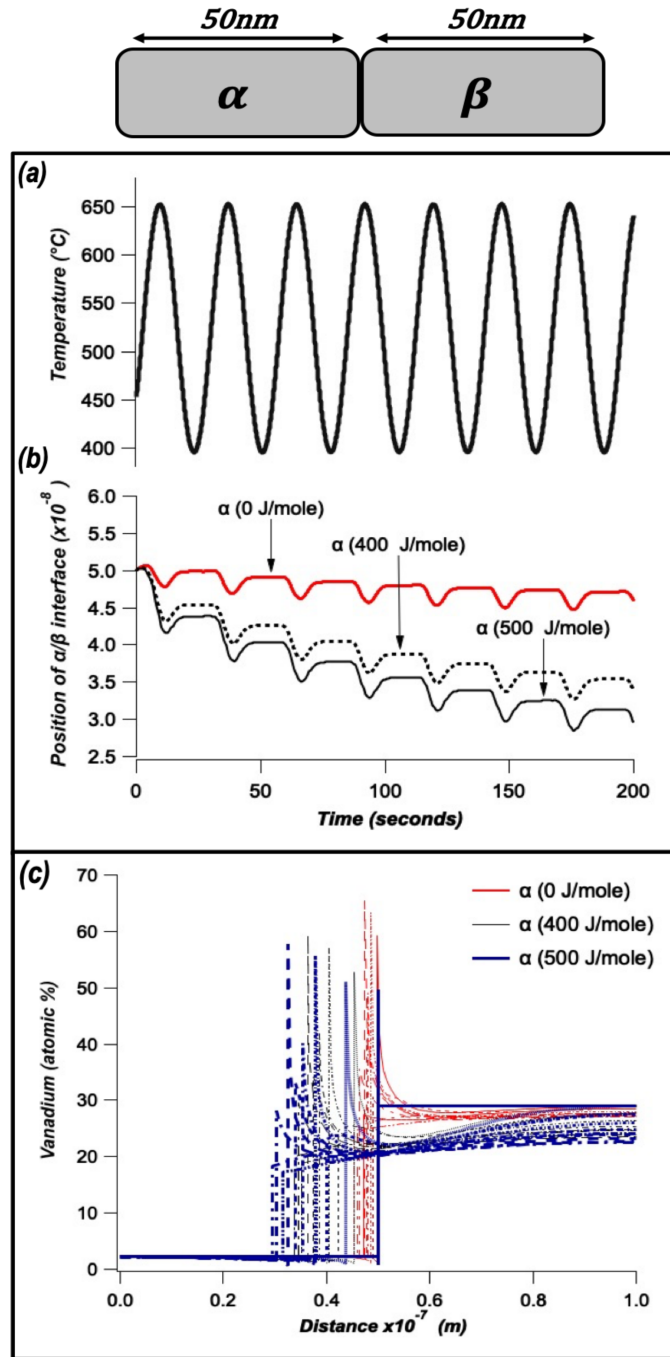


Figure 6.15: DICTRA simulations of the thermo-mechanical cycles. (a) Thermal cycle plot used as input for the simulation; (b) Position of the α/β interface with time, indicating the impact of added stored energy in the α phase; (c) Vanadium concentration (mole-fraction) across the α and β phase.

75cycles samples as discussed in 5.2.3. The FWHM analysis in the above section, clearly indicated strain partitioning effects between α and β , where the strain within the β is saturated and an accumulation of plastic strains occurs in the α phase. Thus, an enhanced α/β interface motion is achieved when plastic strains accumulate within the α phase.

The movement of the interface along with solute re-distribution effects is validated with calculations using a Diffusion based thermodynamic model - DICTRA[®], with the TCTI2 titanium thermodynamic database and the TCTI3 mobility database [141, 162, 163]. DICTRA simulations are run based on the interface concentration profiles and analyses of the 45cycles and 75cycles ex-situ thermo-mechanical analysis, from the previous chapter. The DICTRA simulation is set up by attached a 50nm α block to the left of a 50nm β block. The starting composition of α and β phases are set based on the atom probe data of the reference sample (α : V=2.27 at.% Al=8.33 at.% and β : V=2.09 at.% Al=29.03 at.%). A sine curve is fit to the thermal cycle data and set as the global condition for the simulation. From the previous chapter, our thermodynamic calculations indicated that with an addition of 400 J/mole and 500 J/mole matched the vanadium concentrations of the 45cycles and 75cycles sample respectively.

In order to be able to simulate the effect of stored energy, the homogenization model in DICTRA was enabled [164]. The homogenization model assumes that equilibrium is maintained locally corresponding to the local composition, temperature, and pressure of the phase. The local kinetic properties are found by choosing a then suitable "averaging function" across the phases that can be implemented during a 1D simulation. Enabling the homogenization model for our diffusion calculations, a stored energy is added to the α phase and simulated.

Shown in Figure 6.15 are the time-temperature plot, position of interface plot and the diffusion of Vanadium across the interface plot. Vanadium plays an important role in

the kinetics of phase transformation in the Ti6Al4V alloy system, where lower Vanadium concentrations within the β phase indicates a more stable β . This is clearly seen in [Figure 6.15\(b\)](#) and (c). With an addition of 400 J/mole and 500J/mole to the HCP α phase, the α/β interface movement is much more significant as shown by the blue and black lines. Looking at the Vanadium solute concentration, as shown in [Figure 6.15\(c\)](#), the vanadium is reduced to 20 at% in the β phase, matching the results from our atom probe analysis of the 45cycles and 75cycles sample. On comparison, when subject to just thermal cycles (marked by red lines) between 400 °C and 650 °C, negligible changes in the position of the α/β interface occurs with no change in the Vanadium concentrations across the β phase. This is expected, since the diffusivity of Vanadium is very low and restricted in our TM temperature bounds. This analysis indicated that the strain accumulation during thermo-mechanical fluctuation indeed locally influence the interface equilibrium dynamics.

6.4 Summary

This chapter can be summarized as:

(1) A time resolved study on the elastic/plastic strain partitioning between the α and β phases were examined during in-situ thermo-mechanical cycling experiment using High energy X-rays diffraction at the FAST beamline, CHESS. TM reversals between 400 °C and 700 °C were imposed on an AM Ti6Al4V alloy. Interestingly, as hypothesized earlier, a gradual plastic strain accumulation was noticed from the FWHM analysis in the α phase particularly in the (0002) basal planes. Whereas the β phase showed no effect as seen from the FWHM value throughout the TM cycling, suggesting that the BCC β phase initially takes in the plastic strains, and once saturated, a strain transfer to the α phase occurs. Thermal cycling between these temperature limits showed no impact in both phases.

(2) Nano-scale evaluation and quantification of the effect of plastic strain accumulation on the solute re-distribution of Al and V across the α and β interface was done with Atom Probe Tomography. Vanadium across the β phase in the TM cycled sample reduced to ~ 22 at.% from an initial of ~ 26 at.% (reference sample). This re-distribution of the solute element further confirms the minor increase in the β phase fraction measured during in-situ TM reversals.

(3) Thermodynamic diffusion calculations revealed that the α/β interface movement occur much more significantly when the stored energy within the α is increased, i.e., an increase in the dislocation density within the α phase. This leads to the growth of the β phase, as can be seen from the reduced vanadium concentration across the β . On comparison, when subject to pure thermal cycling between the same temperature range, negligible changes are seen in the interface motion as well as with the solute concentration across the interface. The findings clearly suggest that the microstructure evolution during AM and interface stability's during solid/solid phase transformations are much more dependent on thermo-mechanical signatures rather than just thermal effects.

CHAPTER 7

Conclusion and Future Work

7.1 Conclusion

- (i) *Overarching goal of the study:* The thermo-mechanical-metallurgical interactions of an additively manufactured Ti6Al4V alloy are investigated, with a focus on the spatial and temporal transients of plastic instabilities necessitated by fluctuating thermo-mechanical reversals and their impact on the α/β inter-phase kinetics.
- (ii) *What are the characteristics of the α/β morphologies across different locations in an E-PBF Ti6Al4V cube?* The impact of complex thermal gradients in Ti6Al4V alloy is examined via a investigation on Ti6Al4V cube samples fabricated on an ARCAM (E-PBF) system. The cubes were built with 3 scan strategies - a linear Raster, ordered spot fill and Random spot fill, following which an ex-situ analysis at different locations across the cubes was conducted. The cubes fabricated by the spot fill melt pattern showed a higher concentration of porosities and lack of fusion defects when compared to the raster scan cubes. Microstructural gradients in terms of the α morphologies were noticed along the build direction across the 3 cubes.

(iii) *How does the predicted values of the spread of T , G and V look across a layer of the above Ti6Al4V cube?* A semi-analytical heat transfer model, developed at the MDF, ORNL, is employed to interpret the spread of temperatures (T), thermal gradients (G) and interface velocities (R) across a layer in the build. The predicted G and R values indicated columnar grains as the primary solidification structure which is noticed from the EBSD analysis on the cubes indicating large columnar prior- β grain aligned along the build direction.

(iv) *How do these microstructural variations correlate with predicted values of T , G and V ?* The simulated values and fluctuations of G and R across a layer, predicted by the model, is correlated with the α/β microstructure of the spot melted cubes. Regions at the center of the cube have longer and wider α laths separated by thicker β ribs resembling an α morphology obtained due to slower cooling rates ($\sim 1 \times 10^4$ K/s), which relates back to the shallower thermal gradients experienced at the center of the cube. On the contrary, at the corner of the cube, with larger thermal gradients and faster cooling rates ($\sim 9 \times 10^4$ K/s), the α morphology is more broken down with shorter α laths.

(v) *What is the response of AM Ti6Al4V, subject to imposed thermo-mechanical gyrations?*

Out-of-phase cyclic thermo-mechanical reversal experiments were conducted on a AM Ti6Al4V alloy on a Gleeble[®] thermo-mechanical simulator. Temperature ranges, between 400 °C - 650/700 °C, were selected specifically to emphasize on the impact of thermo-mechanical reversals on the $\alpha \leftrightarrow \beta$ Solid/Solid phase transformations, with alternating compressive and tensile strains amplitudes of 0.8%, 1% and 1.2%. A progressive softening is noticed as the macro stress-strain response from the imposed thermo-mechanical reversals. Samples subjected to rapid TM (30 seconds/cycle)

reversals showed a monotonic increase in the β phase fraction. In contrast, slow TM (300 seconds/cycle) reversals showed unexpected nonlinear behavior of initial increase of β phase fraction followed by decrease. The above differences are attributed to relative strain partitioning between α ($\epsilon=0.01$ in $\alpha(101)$, $\epsilon=0.012$ in $\alpha(002)$ and $\epsilon=0.011$ in $\alpha(100)$) and β phases and subsequent recrystallization derived through diffraction peak width analyses measured by neutron diffraction.

(vi) *How does the α/β interface respond to the macro scale thermo-mechanical fluctuations?*

Nano-scale Atom Probe analysis across the α/β interface indicated a reduction of the Vanadium concentration, from an initial of 30 at.% to 18 at.% in the thermo-mechanically cycled samples. This in-turn straddles the results from the neutron diffraction analysis which showed a doubling of the β phase fraction ($\sim 2.5\%$ in 0cycles to $\sim 5.7\%$ in 45cycles) post thermo-mechanical reversals. Thus, in order to attain local equilibrium at the α/β , a reshuffling of solute atoms at the interface is noticed. The concentration profile at the α/β interface points to a possible reconstructive type of transformation, where the diffusion of Vanadium is enhanced through dislocations, i.e. pipe diffusion. Further, TEM analysis of the thermo-mechanically cycles sample indicated an increased dislocation density in the β phase and a scatter of dislocations across the α phase, adding to our hypothesis of β growth via pipe diffusion.

(vii) *What do Computational thermodynamic models predict?* Thermodynamic calculations

with ThermoCalc[®] software were performed to evaluate the effects of accumulating plastic strains in the α and β phases by the addition of an arbitrary amount of energy, i.e., stored energy. Calculations indicated that an estimated increase of 400 to 500 J/mole (at 650 °C) of stored energy in the α phase is necessary to trigger a $\alpha \rightarrow \beta$ phase transformation.

(viii) *How does the above hypothesis play out during in-situ thermo-mechanical reversals?*

Following the above insights from our ex-situ analysis of the thermo-mechanically cycles samples, In-situ thermo-mechanical reversals were performed at the FAST beamline, CHESS. With the capability of high energy X-ray diffraction, the temporal events of plastic strain partitioning between the α and β phases were captured. FWHM values of the α phase showed an increasing trend indicating that plastic strains accumulated in the α phase during thermo-mechanical reversals, with a major role in the (0001) basal planes. Whereas negligible changes were noticed in the β phase after the first few cycles. These trends indicated that a plastic strain transfer occurs during TM cycling from β to α .

(ix) *Does thermodynamic diffusion models predict the same?* Thermodynamic diffusion calculations (DICTRA[®]) indicated that an excess stored energy in the α phase indeed plays a significant role in the interface movement and partitioning of Vanadium across the β phase. Comparing this to a thermal cycle, negligible changes are noticed in the interface motion and solute re-distribution across the phases. The findings clearly suggest that the microstructure evolution during AM processing is governed by thermo-mechanical fluctuations and that the interface stability's during solid/solid phase transformations are much more dependent on spatial and temporal thermal+mechanical signatures rather than just thermal effects.

7.2 Significance to AM industry

The current work is aimed at going a step further in rationalizing the thermo-mechanical-metallurgical dynamic behavior of an alloy system under complex AM processing conditions. AM processed alloys have shown to have different metallurgical features when compared

to the conventional manufactured route. A major factor into these deviations are the solidification conditions (L/S and S/S dynamics) - that are constantly changing across an evolving geometry during AM processing. Therefore, localized stress and strain fields brought about part-level thermal gradients typical to AM are bound to affect the response of material and thereby changing the local microstructure, as well as their dynamic flow properties. With the growing AM industry with an evolution of different alloy designs and scan strategies for better optimization of part properties, addressing their uncertainties and variations of metallurgical properties of the alloy has been a constant battle. For instance, many reports have proposed different $\beta \rightleftharpoons \alpha + \beta$ transformation sequences in Ti6Al4V on cooling and on subsequent thermal cycles below the solidus temperature. Although significant progress has been made in tracking the evolving spatial and temporal events of temperature during AM processing using Near-Infrared cameras, Neutron and High-energy X-ray diffraction capabilities, the pursuit of the actual phenomenon of parent to product phase transformation kinetics during processing remains. Our thermodynamic and diffusion calculations and experimental results show that these thermo-mechanical boundary conditions will lead to a departure from thermodynamic equilibrium calculations performed with an assumption of zero thermal gradients. Thus, the integration of the micro-scale α/β phase stability kinetics in the presence of local plastic instabilities generated by macro-scale thermo-mechanical gyrations is significant to the physical metallurgy of alloys manufactured via Additive Manufacturing. It is noteworthy to mention that although our thermo-mechanical reversals may not be the same as those observed during AM, this study demonstrates that the assumptions of local equilibrium based solely on thermal boundary conditions alone as well as monotonic history-independent stress-strain constitutive properties assumed may be irrelevant under AM conditions. Overall, this work goes a step further in unraveling the

unique physical metallurgy features of metal Additive Manufacturing as it evolves into the industrial sector as a developing dependable technology.

7.3 Future Work

Based on the current research progress, there are many ‘opportunities to improve’ and ‘unknowns to resolve’ in understanding the physical metallurgy of alloy systems fabricated under AM processing conditions.

Thermo-mechanical response of other alloy systems The interesting aspect of our thermo-mechanical experiments is its repeatability and applicability for understanding the metallurgy in any alloy system. One of the key advances in the realm of metal AM, is the feasibility to fabricate parts with a range of alloy compositions such as Nickel based super-alloys, Stainless Steel alloys, Cobalt alloys, Aluminum alloys, Titanium alloys, High entropy alloys, Gold and Silver. With this development comes the limitation of the unknown complex variables that constrain the solidification and microstructural evolution of AM processed parts. For instance, our above approach can be implemented in Nickel alloys systems where the interactions between the non-equilibrium $\gamma/\gamma'/\gamma''$ phases/precipitates under complex thermo-mechanical reversals have not been addressed. Preferential plastic strain accumulation between phases and/or precipitates in an alloy due to rapid fluctuation of thermal gradients, can lead to the decomposition of the parent $\leftrightarrow$ product phase. Since these phenomenon’s are governed by the topology of the Gibb’s free energy, ultimately there results a competition between different phase transformations such as reconstructive, displacive, interface-controlled and massive transformations, leading to the development of microstructures in AM alloys. In addition, the impact of such studies can also be relevant

to the solidification cracking and defect formation in AM processed parts.

In-situ measurements of thermo-mechanical gyrations In our study, we were able to impose complex thermo-mechanical reversals (compressive and tensile fluctuations) between temperatures of 400 °C and 650/700°C which lies well within the $\alpha+\beta$ region of the Ti6Al4V system, where the diffusivity of solute elements are low. During AM, higher temperature fluctuations may exist leading to a need to address the temporal transients at higher temperatures. In addition, a variety of complex thermo-mechanical signatures (temperatures with varying strain limits) and yet to be addressed. Needless to say, in-situ measurements during AM processing aid in the better understanding of the process (w.r.t. scan strategies, processing variables, energy density and geometry) in terms of the temperature distributions, thermal fluctuations and interpretation of solidification structure (Columnar to Equiaxed Transition) and have been extensively researched. Although, in-situ measurements of the impact of thermal fluctuations due to reversals of large thermal gradients is yet to be addressed and remain a challenge. The current study implemented a design of thermo-mechanical experiments based on published experimental patent by Kotecki et al. (US Patent #US7409869) on a Gleeble[®] thermo-mechanical simulator. With the current enhanced capabilities of high energy diffraction sources and equipped loadframes to apply complex thermo-mechanical boundary conditions, a better understanding of these spatial and temporal transients can be addressed. One such source is the XRD1 beamline at the Brazilian Synchrotron Light Source, that is equipped with a Gleeble[®] simulator.

Integration into Computational AM models Computational modelling of AM processes and alloys is a hot topic in the AM research field. Needless to say, computational modelling of AM process benefits the industry in increasing the success rate of builds by the preemptive

warning of potential defects and cracks. However, due to the complex integration of multiple variables involved during the AM process in conjunction with the limited in-situ experimental data, modelling remains a challenge. Moreover, since it has been much emphasized in AM literature that AM processes lead to the non-equilibrium development of microstructures (phases and precipitates), there occurs a bigger need to address and implement relevant data into microstructural modelling capabilities for a better prediction of AM part properties. Current works are going on in collaboration with the ExaAM group at ORNL to implement the above findings in the microstructural modelling of AM Ti6AL4V.

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Appendices

CHAPTER A

Appendix

APPENDIX 1

ThermoCalc and DICTRA macros:

ThermoCalc Simulation: Simulation of the impact of stored energy on the Vanadium phase boundary (Ti6Al4V ssytem) to corroborate the Atom Probe Analysis of the thermo-mechanically cycled samples.

@@ Addition of stored energy into the α phase

go data

@@ Switching to Titanium data base and appending Mobility database

Sw TCTI2

Def-sys Ti Al V

Rej ph *

Rest ph bcc_b2 hcp_a3

Get

@@ Entering the poly module

Go poly

S-c w(al)=6e-2 w(v)=4e-2 p=1e5 n=1 t=923

C-e

L-e

@@ Adding an arbitrary amount of energy to the β phase

Advanced-options

Phase-addition

bcc_b2

500

@@ Entering the axis variable

S-a-v 1 w(al) 0 1 0.01

S-a-v 2 w(v) 0 1 0.01

map

DICTRA Simulation: Simulation of the interface movement and solute redistribution across the α and β interface when subject to thermo-mechanical reversals (thermal cycles + energy added to α phase).

@@ Redistribution of solute elements during cycling heating and cooling

@@ Starting α and β composition profile measured from APT analysis

go data

@@ Switching to Titanium data base and appending Mobility database

Sw TCTI2

Def-sys Ti Al V

Rej ph *

Rest ph bcc_b2 hcp_a3

Get

App mobti3

Def-sys Ti Al V

Rej ph *

Rest ph bcc_b2 hcp_a3

Get

@@ Entering Dictra module

Go d-m

@@ Set temperature conditions (sine fit to temperature data)

@@ Fitted curve equation: $W_coef[0]+W_coef[1]*\sin(W_coef[2]*x+W_coef[3])$

@@ Fitted Variables: $W_coef=524.04,128.82,0.22855,-0.58596$

Set-cond glob t 0

$273.15+(524.04+128.82*\sin(0.22855*time-0.58596)); *$

N

@@ Entering geometry and grid size

Ent-region alpha

Ent-region beta alpha yes

Ent-grid alpha 50e-9 lin 1000

Ent-grid beta 50e-9 lin 1000

@@ Enter Phase and initial composition

Ent-phase act alpha matrix hcp_a3

Ent-phase act beta matrix bcc_b2 1

Ent-comp alpha hcp_a3 ti m-f

Al lin 8.33e-2 8.33e-2

V lin 2.27e-2 2.27e-2

Ent-comp beta bcc_b2 1 ti m-f

Al lin 2.09e-2 2.09e-2

V lin 29.03e-2 29.03e-2

@@ Set-simulation method to be homogenization

Homo yes yes

@@ set homogenization parameters - adding energy to the α phase

Util-homo

No

No

No
 No
 No
 No
 No
 Yes
 HCP_A3
 500
 NO
 NO
 NO
 YES
 0.001
 NO
 NO
 NO
 NO
 NO
 NO
 NO
 NO
 @@ Setting Simulation Parameters
 200
 Y
 10
 20
 30
 sim

APPENDIX 2

Peak Identification (Mass Spectrum) using IVAS, Atom Probe Tomography Data

Peak identification was done with IVAS, as shown in [Figure A.1](#). Oxygen was primarily present as TiO. This is the general peak identification done for all Atom probe data reported here.

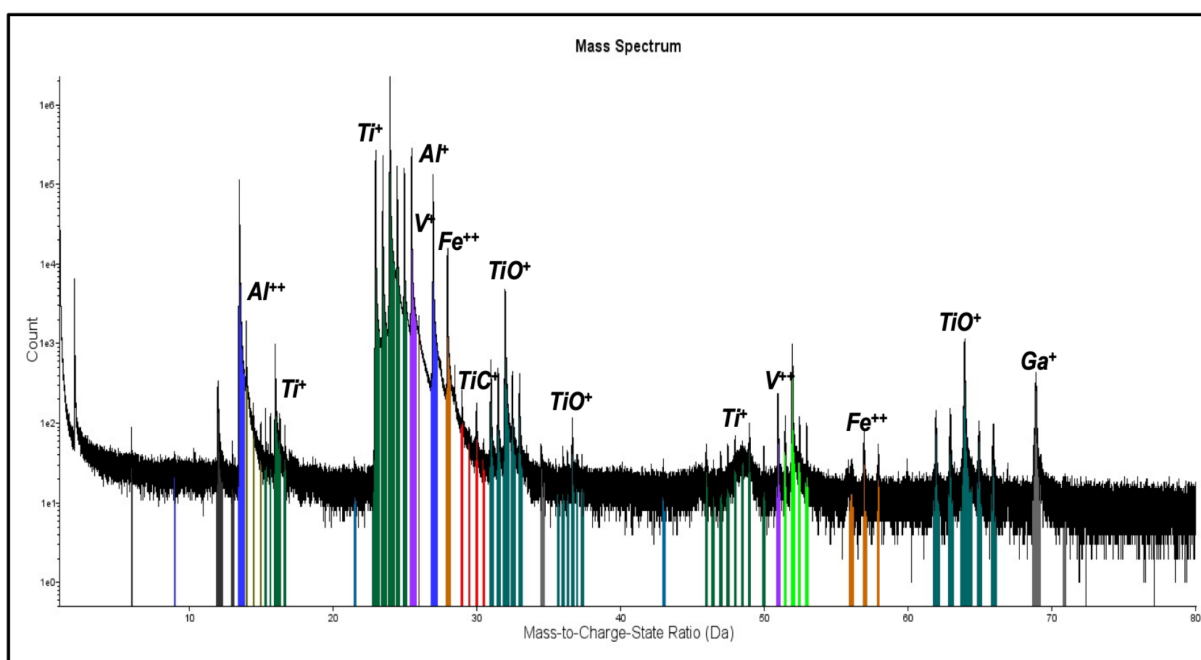


Figure A.1: Peak identification from the Mass spectrum of the Atom Probe Data.

VITA

Sabina Caryl Kumar

Originally from Tamil Nadu, India, Sabina Kumar grew up in Muscat, Oman. She then later on went to continue studying in India, where she completed her undergraduate studies and received her Bachelors of Engineering in Metallurgical Engineering from PSG college of Technology, India. Following this, she took up a job as an engineer in TVS Sundaram Fasteners at Chennai, India and worked as a metallurgist in the R&D laboratory. She then later decided to pursue her graduate studies in the field of Metal Additive Manufacturing where she was able to secure a Graduate Assistantship with Dr. Babu at the University of Tennessee, Knoxville. She completed her Doctor of Philosophy degree in Material Science Engineering with a concentration on the thermo-mechanical-metallurgical aspect of an Additively Manufactured Titanium alloy. Her research interests include characterization, physical metallurgy, phase transformation and mechanical behaviors. She is incredibly grateful for all the support from her husband and family and she steps into new beginnings.