Grain-Boundary Parameters Controlled Allotriomorphic Phase Transformations in Beta-Processed Titanium Alloys

DISSERTATION

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By

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Abstract

Allotriomorphic or grain-boundary alpha (GBα) is an inherent and important microstructural feature of diffusional phase transformations in β-processed titanium alloys. This phase has a negative influence on various mechanical properties, such as high cycle fatigue, fracture toughness, ductility etc. Also, it has a profound influence on the overall microstructural evolution. For example, the nature of the distribution of this phase affects both morphology and crystallography of the adjacent Widmanstätten α. Thus, it contributes to the presence of transformation texture in these materials.

This study is primarily concerned with two main aspects of the evolution of GBα: morphology and crystallographic variant selection. It is known that the grain-boundary (GB) parameters, namely, misorientation angle/axis and the GB plane, have important roles in both aspects. While misorientation angle and axis related to the crystallography of adjacent crystals can easily be determined using diffraction based techniques, an accurate determination of the local crystallographic orientation of the GB plane is difficult because of its three-dimensional nature. To address this issue, two independent experimental approaches have been developed in this study that use a combination of dual beam focused ion beam (FIB), SEM and electron back-scattered diffraction (EBSD) methods. Both these approaches considerably simplify the problem because of a relatively easier experimental set-up and a versatile methodology.
The results of the present study indicate that both in α/β- and β-titanium alloys, variant selection and GB parameters control the evolution of the allotriomorphic α phase. In particular, the misorientation angle/axis parameters control the early precipitation of GBα. The grain-boundaries of those adjacent β-grains that produce nearly parallel <111> and/or <101> poles are the preferred sites for the early nucleation of GBα in β and α/β-titanium alloys. In addition, these closely related poles significantly influence the crystallographic variant selection criterion in a majority of cases contributing to a considerable reduction in the allowed variants of GBα. In contrast, the GB plane orientation controls the variant selection in relatively fewer cases where a high misorientation angle between GBα and the adjacent β-grain that did not establish a Burgers-OR is produced.

The morphology of GBα is generally continuous along the grain-boundaries in α/β–Titanium alloys. Three-dimensionally, this morphology can be represented in terms of the ‘local true thickness’ of a rectangular slab. In contrast, the morphology of GBα in β-titanium alloys can be broadly divided into two categories, ‘discrete’ and ‘continuous’. A continuous morphology is assigned to precipitates with relatively large aspect-ratio, while discrete GBα produce a small aspect ratio. It has been determined that in β-titanium alloys, continuous GBα precipitates are produced when the GB plane orients nearly perpendicular to [1 1 1]ρ ||[2 1 0]α of the contributing Burgers-OR. In case of α/β-titanium alloys, the phenomenon of the thickening of GBα is even more restricted. The thickening of GBα is higher when the GB plane orients close to the broad-face or the
habit plane ([1 1 1]_β) of the Burgers-OR. It has been proposed for the first time that the crystallo-
graphic and morphological aspects of GBα and adjacent Widmanstätten α are interrelated and primarily dictated by the GB parameters. Specifically, once a particular crystallo-
graphic variant of GBα is chosen by a set of criterion, the crystallographic and morphological nature of adjacent Widmanstätten α is also predicted. The resulting Widmanstätten α morphology in combination with the nature of the GB plane would control the growth (continuous or discrete) of GBα.

Finally, transmission electron microscopy studies have revealed a variation in the interfacial structure between GBα and the adjacent β grain different from previously known well-defined interfacial structure between Widmanstätten α and the parent β phase. The faceting of the interface as well as presence of new sets of misfit dislocations have been observed in this work.
Dedication

This document is dedicated to my dear grandparents, parents, siblings, wife and daughter.
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Publications

• P.C. Collins, S. Koduri, V. Dixit and H.L. Fraser, “On the use of neural networks to develop an understanding of the roles of continuum, microstructural, and compositional variables on the fracture toughness of α/β-processed TIMETAL®6-4”, Submitted in Metallurgical and Materials Transactions A
• B.A. Welk, H.L. Fraser, V. Dixit, T. Williams and M.A. Gibson, “Phase Selection in a Laser Surface Melted Zr-Cu-Ni-Al-Nb Alloy”, Submitted in AMPT conference, Australia


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**Fields of Study**

Major Field: Materials Science and Engineering
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Chapter 1
Introduction

Titanium alloys offer an excellent combination of properties, such as, high strength to weight ratio, good fracture toughness and fatigue resistance, good corrosion resistance, bio-compatibility etc. As a result these alloys have found extensive applications in both commercial and strategic sectors.

Depending upon the thermo-mechanical treatment, a wide variation in the microstructures and properties can be produced in these alloys. The $\alpha+\beta$ processing leads to a production of microstructures consisting of globular $\alpha$ and the transformed $\beta$. The $\beta$-processed microstructures consist of primary intra-granular and Widmanstätten $\alpha$ laths, secondary $\alpha$ and grain-boundary $\alpha$ layers. Consequently, two distinct morphologies of intra-granular $\alpha$ can be produced in the grain-interior. Fast-cooling from a $\beta$-annealing temperature produces a basketweave microstructure. In contrast, slow cooled microstructures consist of large colonies of $\alpha$ platelets, separated by $\beta$-ribs. The high temperature $\beta$ phase has as a body-centered cubic crystal structure and the low temperature $\alpha$ phase has a hexagonal close-packed structure. From the crystallographic perspective, these phases are often found in a Burgers orientation relationship.

The heterogeneous precipitation of GB$\alpha$ from the $\beta$ matrix at various grain-boundaries and triple points is unavoidable in diffusional transformations in both $\alpha/\beta$- and $\beta$-titanium alloys. This phase non-randomly selects only few of the possible twelve
crystallographic variants while establishing a Burgers-OR with one of the adjacent β grains. This causes the allotriomorphic phase to exercise a long range influence on the development of both microstructure and the transformation texture. Also, the nature of the distribution of this phase can influence the evolution of adjacent Widmanstätten α platelets. This phase also has a deleterious influence on various properties e.g. tensile ductility, fracture toughness and high cycle fatigue.

A number of studies have been conducted to try to understand the possible role of grain-boundary parameters (misorientation angle/axis and orientation of the grain-boundary (GB) plane) on the variant selection by GBα. Some studies have reported the importance of the GB plane, while others have highlighted the role of the misorientation angle/axis. Evidently, there exists a need to evaluate the contribution of all of the GB parameters so that a relative importance of various factors can be established.

There have been isolated attempts to understand the thickening and morphology of GBα. To a large extent, such efforts have focused on the thermodynamic and kinetic aspects of the diffusional phase transformations. What is needed now is to understand and quantify the morphological aspects of GBα relative to GB parameters and variant selection in order to understand the involved mechanism(s).

Very few studies that have looked at the role of grain-boundaries in microstructural evolution and properties in different materials systems, have actually quantified the influence of the GB plane. The main reason for the dearth of such efforts has been the lack of simple methods to determine the orientation of the GB plane because of its three-dimensional nature. Traditionally, transmission electron microscopy has been
used, which is both time-intensive and expensive. The development of novel tools in the last decade, namely, dual-beam focused ion beam (FIB) and electron back-scattered diffraction (EBSD) provides an opportunity to develop methodologies to characterize complete GB parameters with a significant ease.

It is well known that in the grain-interior, the presence of Burgers-OR between $\alpha$ and $\beta$ phases decides the major growth direction as well as the defect structure of the interphase interface. In the case of allotriomorphic $\alpha$, the presence of grain-boundaries forces this phase to grow along a direction different from that of the invariant line and produce a morphology that cannot be predicted by the crystallography. It is therefore expected that the interfacial structure between GB$\alpha$ and the $\beta$ grain that produces a Burgers-OR, would be significantly different from that between Widmanstätten $\alpha$ and $\beta$. In particular, a change in the orientation of the GB plane relative to the selected variant of Burgers-OR and a deviation of GB$\alpha$ and $\beta$ phases from the exact Burgers-OR would result in a variation the interfacial structure. There is lack of information in literature on this topic.

This work is an attempt to explore the influence of misorientation angle/axis and the GB plane on crystallographic variant selection, together with their combined contributions to the morphology of GB$\alpha$ in $\alpha/\beta$- and $\beta$- titanium alloys. For this purpose, two simple and versatile methods for determining the crystallographic orientation of an interface have been developed. In addition, a variation in the interfacial structure between GB$\alpha$ and $\beta$ matrix in the Burgers-OR has been analyzed for the different crystallographic orientations of the GB plane.
Chapter 2
A Literature Survey of Allotriomorphic Phase Transformations in Titanium Alloys

2.1 Abstract

Allotriomorphic $\alpha$ is an unavoidable microstructural feature in $\alpha/\beta$- and $\beta$-titanium alloys because of a high propensity for heterogeneous precipitation at various grain boundaries during diffusional phase transformation. This phase has an important influence on the microstructure, transformation texture and various mechanical properties. Its evolution is affected by the chemical segregation, grain boundary characteristics and the Burgers orientation relationship (OR) between the $\alpha$ and $\beta$ phases. In addition to the misorientation angle/axis and the crystallographic orientation of the grain boundary (GB) plane have significant roles on variant selection and morphology. The microstructural evolution in the grain-interior is also dependent on this phase because of variant selection and adoption of the same variant by the adjacent Widmanstätten $\alpha$ colony present at the prior-$\beta$ grain that establishes a Burgers orientation relationship. However, despite various experimental observations that suggest the importance of the GB plane, very few studies have actually quantified it. The advent of advanced characterization tools such as dual beam focused ion beam (FIB), electron energy-loss spectroscopy (EELS) and electron dispersive spectroscopy (EDS), electron back-scattered diffraction (EBSD) etc. provides an opportunity to advance the understanding of the evolution of these grain boundary $\alpha$ precipitates. These tools
significantly simplify the methodology to determine the site-specific morphology of allotriomorph \( \alpha \), and its crystallographic relationship with other important phases.

### 2.2 Introduction

Titanium based alloys possess an excellent combination of low modulus, high strength to weight ratio, excellent corrosion resistance and bio-compatibility and thus have found extensive applications in the aerospace, medical, and recreation sectors etc [1]. When subjected to various thermo-mechanical processing and thermal treatments, a significantly varied microstructural evolution and therefore properties can be produced [1-3]. It has been observed in various metallic and alloy systems that the heterogeneous formation of grain boundary precipitates in transformations involving a diffusional nucleation and growth cannot be avoided [4]. Not only does such a phenomenon contribute to the microstructural redundancy, in many cases it actually degrades various properties of interest [3, 5-7]. Microstructural redundancy can be defined as the lack of any gain in various properties of interest as result of the phase transformation occurring preferentially at the grain-boundaries in comparison to that in the grain-interior. In titanium alloys the presence of grain boundary \( \alpha \) (GB\( \alpha \)) is known to negatively influence ductility, high cycle fatigue (HCF) and fracture toughness [1-3]. More importantly, this phase affects both morphology and crystallography of adjacent intra-granular \( \alpha \) precipitates [8].
Various microstructural features that are frequently present in titanium alloys are also common in steels. In fact the nomenclature scheme adopted for various α precipitates in titanium alloys has been borrowed from that originally developed for proeutectoid steels by Dube et. al. [9]. In this terminology, the α phase that grows preferentially along the grain boundaries is termed as allotriomorphic α. As opposed to idiomorphic intra-granular precipitates, allotriomorphic α is characterized by an external shape that is not representative of its crystalline symmetry as it is influenced by the grain boundary interface [10]. Despite being an inherent and important microstructural feature, much less effort has been made to understand the allotriomorphic transformations in titanium alloys, compared to that in steels [9, 11-12]. Therefore the contributions of various factors such as grain boundary parameters, chemical segregation and variant selection etc., are less well understood.

This chapter aims to highlight the current state of the understanding of crystallographic and morphological aspects of allotriomorphic α in titanium alloys. The approach used in this discussion involves introducing the physical metallurgy of titanium alloys, followed by the associated diffusional phase transformation from the thermodynamic and kinetic standpoint. Subsequently, the important factors that could influence this transformation, such as Burgers orientation relationship and grain boundary parameters are introduced and a summary of the interfacial structure of these precipitates, as well as Widmanstätten α plates, will be given. Finally the role of allotriomorphic α on both intra-granular microstructural evolution and various mechanical properties, will be given.
2.3 Fundamental and Microstructural Aspects of Titanium and its alloys

2.3.1 Pure Titanium [1, 13]

Titanium is a transition metal with atomic number 22. It has an incomplete 3d orbital and easily forms a substitutional solid solution with elements that have atomic diameter within ±20 % of that of titanium. The melting point of pure Ti is 1678°C and it undergoes an allotropic phase transformation at ~882°C. The low temperature ‘α’ phase possesses a hexagonal close packed (hcp) structure (space group: \( P6_{3}mmc \)). Lattice parameter values of ‘a’ and ‘c’ for this phase are 0.295 nm and 0.468 nm respectively (Figure 1a). Therefore the c/a ratio is 1.587, which is less than the ideal value of 1.633. On the other hand, β phase exists above 882°C at 1 atmospheric pressure, and possesses a body centered cubic (bcc) structure (space group: \( \text{Im} \bar{3}m \)). The lattice parameter of bcc unit cell is 0.332 nm at 900°C (Figure 1b). It has a more open structure than the α phase. Therefore it has larger configurational entropy, making it a more stable phase at high temperatures.

2.3.2 Crystallographic Properties [1]

As clear from Figure 1, the hcp structure of α phase is significantly more anisotropic than the high temperature bcc ‘β’ phase, and leads to the anisotropic elastic behavior of the single crystals of α titanium. The highest value of Young’s modulus of 145 GPa is achieved when the stress is applied parallel to the c-axis and the smallest value (100 GPa) is achieved for the stress direction perpendicular to it (Figure 2). In case
of β-stabilized alloys that retain metastable ‘β’ phase even at room temperature, the value of elastic modulus has been found to vary between 70-90 GPa.

The most important mode of plastic deformation in α+β and β titanium alloys is the dislocation slip on relatively close packed planes and directions. Figure 3 shows the important slip planes in α phase. Here, the slip activity can be of either a type ($b = \frac{120}{\sqrt{3}}$) on (0001), {10\overline{1}0} and {10\overline{1}1} planes, or ‘c+a’ type ($b = \frac{123}{\sqrt{3}}$) that acts on \{10\overline{1}2\} planes. The activation of ‘c+a’ type (or pyramidal) slip is far more difficult than basal and prismatic (a type) slip. In the β phase a dislocation motion could activate on \{110\}, \{123\} and \{112\} planes with Burgers vector $b = \frac{11}{\sqrt{3}}$. Therefore in all, 48 slip systems can possibly get activated in the β phase.

### 2.3.3 Alloy Classification [1,13]

Titanium interacts with a host of other elements. In low concentrations, most of the elements make a solid solution and significantly alter the allotropic phase transformation temperature. Species such as Al, O, C, N increase the β-solutionizing temperature and are termed as α stabilizers. These are in general simple elements, and species such as O and N readily form interstitial solid solutions with Ti. Elements Sn and Zr do not alter the α to β transition temperature even though both are termed as α-stabilizers. Sn replaces Al in Ti₃Al precipitates that get produced when the weight fraction of Al in Ti is more than 6% in the binary alloy system. Zr, like Ti, has an ‘hcp’
structure and can replace it in a multi-component alloy. The effectiveness of these alloying elements has been expressed in terms of Al-equivalency. It is defined as:

$$[\text{Al}]_{\text{eq.}} = [\text{Al}] + 0.17 [\text{Zr}] + 0.33 [\text{Sn}] + 10 [\text{O}]$$

On the other hand species such as Fe, V, Mo, Nb, Fe, and Cu etc., decrease the $\beta$-$\alpha$ transition temperature and are called $\beta$ stabilizers. Most of these elements are transition or noble elements. Also notably, hydrogen is a $\beta$ stabilizer. Figure 4 shows a broad categorization of binary phase-diagrams that exist between Ti and different alloying elements [1]. In general, these alloys make two kinds of phase systems, $\beta$-isomorphous and $\beta$-eutectoid-elements appearing towards the right side of the transition metal period have a higher tendency to make a eutectoid system. Thus, V, Nb, Mo etc. produce $\beta$–isomorphous, and Fe, Cr, Cu etc. make $\beta$–eutectoid alloy-systems. Phase transformations involving eutectoid reactions generally exhibit less solubility in titanium. Also, an addition of a $\beta$-stabilizing alloying element leads to a reduction in the martensite start (Ms) temperature and eventually beyond a certain concentration the martensite formation is completely suppressed and $\beta$-phase gets stabilized. The efficacy of various alloying elements is different with respect to the stabilization of $\beta$-phase. This dependence has been expressed in terms of equivalent Mo-content and it serves as a guiding rule for the $\beta$-stabilizing capacity of various alloying elements.

$$[\text{Mo}]_{\text{eq.}} = [\text{Mo}] + 0.2 [\text{Ta}] + 0.28 [\text{Nb}] + 0.4 [\text{W}] + 0.67 [\text{V}] + 1.25 [\text{Cr}] + 1.25 [\text{Ni}] + 1.7 [\text{Mn}] + 1.7 [\text{Co}] + 2.5 [\text{Fe}]$$
The equations expressed above are, and should only be used, as a qualitative guide because in general, interactions amongst various alloying elements exist and lead to a deviation from the expected behavior. For example, in the presence of oxygen the solubility of Al decreases to ~4.5 wt% from 6 wt% and precipitation of Ti₃Al phase occurs. In the presence of V though, the solubility limit increases to ~5 wt% as the presence of V in solid solution increases the c/a ratio of the α phase [14]. Such interactions significantly contribute to the issues encountered in the quantification of the influence of a given alloying element in a multi-component alloy system.

Depending upon the type and the amount of alloying additions, three different kinds of alloys can be produced. These are called α-, α/β- and β- alloys for the low, medium and high concentrations of β-stabilizing alloying additions. α–alloys consist of ‘hcp’ phase, and therefore are suitable for cryogenic applications. β–alloys on the other cannot be used for such low temperature applications because of the presence of the ductile-to-brittle transition temperature. Nevertheless, depending upon the processing, they can produce higher strength, fracture toughness and fatigue life as compared to α– and α/β– Ti alloys. On the other hand, α/β–alloys show the stability of both α and β phases at room temperature and possess both high strength as well as ductility. In both α/β–alloys and β–alloys, performing various thermo-mechanical processing and heat-treatments can produce a wide variation in microstructure and thus properties.
2.4 Thermo-Mechanical Processing [1]

Thermo-mechanical processing in titanium alloys can be divided into two categories: $\alpha+\beta$ processing and $\beta$ processing. $\alpha+\beta$ processing involves homogenization in the $\beta$ phase field followed by a controlled cooling to room temperature. Subsequently, the material is subjected to deformation in the $\alpha+\beta$ phase regime (Figure 5). Finally, the recrystallization of globular (or equiaxed) $\alpha$ occurs at triple points and (sub) grain boundaries upon heating the material into the $\alpha+\beta$ phase field. Depending upon the deformation rate and temperature as well as the recrystallization temperature, a wide variation in the size distribution and volume fraction of globular $\alpha$ can be achieved. The remaining $\beta$-phase transforms into the lamellar microstructure. As example of a typical microstructure produced by this process is shown in Figure 6 [15].

As shown by the schematic in Figure 7, $\beta$ processing involves an initial homogenization of a given material in the $\beta$ phase and subsequently cooling at a controlled rate to room temperature. It is then deformed in the $\beta$ or $\alpha+\beta$ phase field. Finally it is annealed in the $\beta$ phase regime and is finally cooled to room temperature at different cooling rates. Figure 8 shows an example of the resulting well-developed microstructure in a Ti-5111 alloy where the presence of allotriomorphic $\alpha$ at the grain-boundaries and large colonies of Widmanstätten $\alpha$ colony in the grain-interior is observed. In the present work, $\beta$-processed microstructures have been studied in a greater detail. Therefore it would be useful to understand some aspects of microstructural evolution produced by this thermo-mechanical treatment.
2.5 Evolution of Microstructure and Texture in β-processed Titanium alloys

As shown in Figure 9, during the early stages of the formation of α from the parent β phase, heterogeneous nucleation preferentially occurs at grain-boundaries and triple points. This phase is generally termed as allotriomorphic or grain-boundary α (GBα). Subsequently, this transformation proceeds into the grain-interior, where depending upon the heat treatment a wide variation in morphology and scale of α precipitates can be produced, which is controlled by the cooling rate from the β-annealing temperature. Figure 10 shows a variation in the morphology of intra-granular α produced at different cooling rates. At slow cooling rates, a colony microstructure evolves. It changes to basketweave morphology at high cooling rates as a result of the nucleation of various crystallographic variants in the grain-interior. Colony microstructure mainly consists of GBα precipitates and large colonies of Widmanstätten α side plates separated by fine β ribs and a substantially small fraction of intra-granular α precipitates. In these microstructures the precipitation of GBα has a large influence on the overall microstructural evolution. For example, the crystallography of GBα gets adopted by the adjacent Widmanstätten α colony that is produced on the β-grain that establishes a Burgers-OR (Figure 11). This phenomenon leads to the presence of transformation texture. At high cooling rates the fraction of intra-granular α plates significantly increases and a significantly refined microstructure gets produced. Intra-granular precipitates are identified as those precipitates that do not get influenced by GBα during their evolution.
Thermo-mechanical processing produces a texture in the titanium alloys. Texture can be defined as the phenomenon in which a high population of grains in a polycrystalline material prefers to orient along certain crystallographic directions. The presence of texture leads to an anisotropic mechanical behavior, especially Young’s modulus, tensile properties, toughness etc. In a random microstructure, an average response would be registered. An example of the role of thermo-mechanical processing on the texture in the β-phase is shown in Figure 12. Here, the β-texture in as-received forged billet of Ti-17 alloy has been determined using neutron diffraction [16 below. Apparently in the as-received sample (O), the β phase texture is dominated by a (110)<112> orientation. Upon heating into the β-phase regime (Sample A’), the (110) orientation disappeared and a weak (111) orientation evolved. On the other hand, after forging in the β-phase field (sample-B), a very strong (111)<-1-12> component was produced. In the present work, all of the samples that have been studies have been supplied by TIMET and have been subjected to similar processing steps in the as-received conditions. Subsequently, all samples have been β-annealed and cooled at different cooling rates.

Some of the direct implications of a variation in texture of the β-phase are a variation in the grain-growth characteristics [17] and texture in the precipitated α phase [19].
2.6 Thermodynamics of the Precipitation of Allotriomorphic $\alpha$ from $\beta$ [4]

The fundamental equation to derive the expression for the homogenous nucleation of nuclei of critical radius, $r^*$, of the product phase is taken from Gibbs. The change in the free energy in the system is expressed as,

$$\Delta \gamma = -\nabla V + \gamma \nabla + \gamma \nabla V$$

For a spherical nucleus,

$$r^* = \frac{\gamma \nabla}{(\Delta \gamma - \gamma \nabla)}$$

where, $\Delta \gamma$ is the volume free energy, $\Delta \gamma$ is the volume strain energy, $\gamma$ is the interfacial energy and $A$, $V$ are the interfacial area and volume of the nucleus respectively. Clearly, the presence of isotropic strain energy increases the size of the critical radius in the case of homogenous nucleation. However in general, a homogenous nucleation in a solid-solid transformation reaction is difficult. Almost all of such transformations are heterogeneous in nature owing to the fact that the critical excess free energy required to induce a transformation is significantly lower. The order of the propensity for nucleation of second phase at various sites is, in decreasing order (a) the free surface, (b) triple-points, grain-boundaries and inter-phase boundaries, (c) dislocations, (d) stacking faults and (e) homogenous nucleation sites.

At grain-boundaries, the optimum size of precipitate that minimizes the interfacial energy between precipitate and matrix phase and the resulting shape is shown in Figure
13. The reduction in activation energy for a heterogeneous nucleation at a grain-boundary relative to a homogenous nucleation in the grain-interior is given by,

$$ \frac{\Delta G_{\text{het}}}{\Delta G_{\text{hom}}} = S(\theta) = \frac{2 + \cos \theta (1 - \cos \theta)}{2} $$

Where,

$$ \cos \theta = \frac{\gamma_{\beta\gamma}}{2\gamma_{\gamma\beta}} $$

This equation shows that the critical radius of a nucleus for same at both homogenous and heterogenous nucleation. However, there is a significant reduction in the activation barrier at grain-boundaries, which promotes a preferential precipitation of the second phase at such locations.

In case of titanium alloys, there is a change in crystal structure from bcc (β phase) to hcp (α phase). Lee et. al. [22-23] showed that a significant decrease in the activation barrier could be achieved by suitably orienting the two crystal structures, so as to produce a semi-coherent interface. Such a phenomenon leads to decrease in the net sum of interfacial and strain energy. Therefore, there exists a driving force for the α phase to attain an orientation relationship with parent β phase to maintain a low energy configuration. As it will be discussed in this work, the presence of orientation relationship has an extremely important role in evolution of allotriomorphic α and affects its morphology and crystallography.
2.7 Orientation Relationships between $\alpha$ and $\beta$ and Variant Selection at the Grain-Boundary

In case of transformations involving bcc-hcp crystal structure transition, three main types of orientation relationships have been mentioned in literature. These are Burgers [24], Potter [25], and Pitsch-Schrader [26] orientation relationships (Table 1).

With regard to the titanium alloys however, generally Burgers and Potter orientation relationships have been experimentally observed between $\alpha$ and $\beta$ phases [27-32]. Interestingly, there exists only a small angular deviation of 1.63° about common $\langle 1 \overline{1} 0 \rangle \alpha \parallel \langle 1 \overline{1} 0 \overline{0} \rangle \beta$ to attain one orientation relationship from another [33]. It causes a reasonable possibility of producing either of these two orientation relationships in both cases of intra-granular as well as grain boundary precipitates.

<table>
<thead>
<tr>
<th>Orientation relationship</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burgers orientation relationship</td>
<td>${110}<em>\beta \parallel (0001)</em>{\alpha}, \langle 1 \overline{1} \overline{1} \rangle_\alpha \parallel \langle 1 \overline{1} 0 \overline{0} \rangle_\beta$</td>
</tr>
<tr>
<td>Potter orientation relationship</td>
<td>${110}<em>\beta \parallel {1 \overline{1} 0 \overline{1}}</em>{\alpha}, \langle 1 \overline{1} \overline{1} \rangle_\alpha \parallel \langle 1 \overline{1} 0 \overline{0} \rangle_\beta$</td>
</tr>
<tr>
<td>Pitsch-Schrader relationship</td>
<td>${110}<em>\beta \parallel (0001)</em>{\alpha}, \langle 0 0 1 \rangle_\alpha \parallel \langle 1 \overline{1} 2 0 \rangle_\beta$</td>
</tr>
</tbody>
</table>

Both experimental and simulation studies on various titanium alloys have shown that intra-granular $\alpha$ precipitates prefer a near Burgers orientation relationship with the parent $\beta$ phase [27-29, 32]. However, a few experimental studies [30-32] of the evolution
of GBα in all titanium alloys and intra-granular α in certain titanium alloys with relatively higher content of β-stabilizers (Ti-22V-4Al, Ti-Cr and Ti-40(wt%) Mo alloy systems), have found the presence of Potter relationship in some cases, in addition to Burgers orientation relationship. In particular, Furuhara et. al [30] has observed the presence of both orientation relationships between GBα and adjacent β-grains. In general, GBα tends to deviate from the exact Burgers-OR in an attempt to produce a compromise between both adjacent grains (Figure 14)[30]. Both Burgers and Potter orientation relationships have been shown [30] to produce stable interfacial structures consisting of structural ledges and misfit dislocations. From the experimental standpoint though, a small difference in these two orientation relationships makes it difficult to distinguish them and careful angular measurements between [110]β and [0001]α is necessary. To summarize, both Potter and Burgers orientation are possible. However, most of the literature has shown the preference for Burgers OR except for a small number of cases where the presence of the Potter OR has been shown. At the grain-boundaries, the probability of producing either of the orientation relationship is relatively higher. While Burgers-OR is always preferred between Widmanstätten α and β, Potter OR has been known to occur occasionally between GBα and one of the adjacent β grains. It is speculated that a misorientation between two adjacent β grains plays a role in producing this small deviation from the exact Burgers-OR.

Figure 15 shows a schematic of the Burgers-OR where (0001) plane of α phase, which is the close packed plane gets aligned with the one of {110} plane of β phase (
(110)\(\beta\) \(\parallel\) (0001)\(\alpha\). In addition, one of the close packed direction of \(\beta\) phase gets aligned with one of the close packed directions of hcp phase namely, \([1\bar{1}1]_\beta \parallel [1\bar{1}20]_\alpha\). These conditions decide the crystallographic orientation of the broad face of the \(\alpha-\beta\) interface, which is 14° away from \([1\bar{1}2]_\beta \parallel [01\bar{1}0]_\alpha\) [34]. As there are six equivalent \{110\} planes in the given \(\beta\) phase, and for each plane two different variants of \(\alpha\) are possible. It makes twelve possible variants of \(\alpha\) precipitates equally likely in the grain-interior. The corresponding interfacial structure of the broad face enforced by the Burgers-OR and lattice parameters of \(\alpha\) and \(\beta\) phases in the grain-interior has been schematically shown in Figure 16. Phase field modeling studies have also been used to explain the presence of interfacial structure at the \(\alpha-\beta\) interface [35] (Figure 17: polar plot shows the minimum energy configuration along the broad face or habit plane for a Burgers-OR between \(\alpha\) and \(\beta\) phases in titanium alloys [32].

With regard to the precipitation of second phase at the grain-boundary, the presence of an orientation relationship between the allotriomorphic phase and at least one one of the adjacent matrix grains was proposed by Smith et. al. [36] and many other studies [37-39] have also confirmed this phenomenon. As it has been discussed earlier, the nucleation and growth of second phase is highly favored at the grain-boundaries. Theoretical calculations based on the minimization of the activation energy for the critical nucleus formation at the grain boundary have predicted the preference for a minimum angle between low energy planes and GB plane [40-41]. In other words, the orientation of the GB plane with respect to low energy planes has been given a significant
importance with regard to the nucleation of product phase. For example, in duplex stainless steels, the formation of $\gamma$ (fcc) phase at the grain-boundaries in $\alpha$ (bcc) matrix have shown the presence of Kurdijumov-Sachs orientation relationship, wherein \{111\} plane of $\gamma$ phase that lied parallel to \{110\} plane of $\alpha$ phase, showed a minimum deviation from the grain-boundary plane for one of the grains [39]. It was also shown that a particular variant got selected as a result of the preference for maintaining a smallest deviation from the close packed plane of the opposite grain. This phenomenon is termed as ‘variant selection’ where a particular orientation relationship is preferred over other equivalent variants.

A similar exploration done on GB$\alpha$ precipitates in Ti-Cr alloy system by Furuhara and Aaronson revealed that these precipitates maintain a near Burgers orientation relationship with one of the neighboring prior-$\beta$ grains [42]. With respect a both adjacent $\beta$ grains, twenty four variants of $\alpha$ precipitates are probable. Interestingly, it was found that instead of maintaining a low misorientation from low energy planes, grain-boundary appeared to select those variants of $\alpha$ phase for which the $[1 \bar{1} 1]_{\beta} \parallel [11 \bar{2} 0]_{\alpha}$ lied on the trace of grain-boundary (Figure 18). Further, a unique variant of GB$\alpha$ gets selected during an attempt to maintain a good coherency with the non-Burgers $\beta$ grain [30]. The presence of misfit dislocations on the interface between GB$\alpha$ and $\beta$ grain (that does not establish a Burgers-OR) support this view. These observations indicate that probably both $(110)_{\beta} \parallel (0001)_{\alpha}$ as well as $[1 \bar{1} 2]_{\beta} \parallel [0 \bar{1} 10]_{\alpha}$ of the Burgers-OR are appreciably low energy planes in comparison to $[1 \bar{1} 1]_{\beta} \parallel [11 \bar{2} 0]_{\alpha}$ direction. Thus
any orientation of grain-boundary plane lying between these two perpendicular direction (and containing the \([1\overline{1}1]_p \parallel [11\overline{2}0]_\alpha\) growth direction) would contribute to low interfacial energy at the grain-boundary. In addition the nature of deformation induced defects was also found to affect the phenomenon of variant selection and modify the rules [43]. It should be noted from these studies that these observations with respect to the orientation of grain-boundary plane are statistical in nature and a deviation from these observations is possible. Whereas, studies conducted by Stanford et. al. [44] have highlighted the importance of misorientation angle/axis. They showed that the closeness of \(<101>\) poles of the adjacent grains contribute significantly to the variant selection (Figure 19). However, there exists in literature a lack of a unified attempt to evaluate the contribution of all GB parameters. It is expected that a combination of misorientation angle/axis and GB plane would control the evolution of \(\alpha\) phase in these materials.

2.8 Grain-Boundary Parameters [4]

As evident from the previous discussion, grain-boundary parameters may have a significant role on the selected crystallographic variant of Burgers-OR. In addition, the geometrical aspects of the grain-boundary could also influence the morphology of GB\(\alpha\) and therefore it is useful to summarize these features. A complete macroscopic description of a grain-boundary requires five independent parameters. Here, two parameters each are contributed by the GB plane and the misorientation axis, and one parameter is provided by the misorientation angle.
**Misorientation angle/axis**

Misorientation angle and axis are related by the crystallographic symmetries of adjacent crystals and can be easily determined by diffraction techniques e.g. TEM, EBSD and x-ray diffraction. The minimum misorientation angle or disorientation angle is generally used to define the energy of the grain-boundaries, which divides a general a grain-boundary into two general types: low angle grain boundary and high angle grain boundary. Low angle grain-boundaries can be described by the dislocation model wherein dislocations are separated by a certain distance \( D = \frac{b}{\theta} \), \( b \): Burgers vector, \( \theta \): Misorientation angle) in an otherwise defect free interface. As the misorientation angle between adjacent grains increases the grain-boundary energy increases and achieves saturation because of the fact that the separation of misfit dislocations decreases at higher misorientation angles. Beyond a certain angle, their stress fields start to interfere and eventually the predicted grain-boundary energy becomes independent of misorientation (Figure 20). At high misorientation angle, a low energy configuration can still be achieved. The measured GB energies in Figure 21 show the presence of cusps [45] that indicates that for certain misorientation angles, grain-boundary achieved a low energy configuration. This phenomenon has been explained by co-incidence site lattice (CSL) model. In this model, two inter-penetrating lattices at a given misorientation angles are evaluated with respect to the matching of lattice points [46]. The locations of local minima correspond to a high extent of the coincidence of the atoms of adjacent grains. A lattice constructed by joining these common points is termed as a coincidence-site lattice (CSL). The fractions of lattice points that belong to CSL are denoted by \( 1/\Sigma \) where \( \Sigma \) is
the coincidence site lattice density. Evidently, smaller is the value of \( \Sigma \) higher is the degree of order in the CSL. The concept of CSL has become very useful in the field of interfaces, and it has shown a correlation of grain-boundary character with host of other properties such as, diffusivity [47], chemical segregation [48-49] etc.

**Grain-Boundary Plane**

We know that a complete description of a grain-boundary character consists of five degrees of freedom. The concept of angle/ misorientation axis discussed above takes into account only three independent parameters and remaining two parameters belong to the orientation of the GB plane. GB plane is entirely a geometrical aspect of a grain-boundary. A three-dimensional nature of this feature has made it a tedious task experimentally to determine its crystallographic orientation and has added to uncertainty in the CSL analysis [50]. A number of methods have been developed in this regard. While most of the earlier approaches are based on TEM [51-52], serial-sectioning based approaches that combine optical microscopy and EBSD methods have also been developed in last twenty years [53-54]. An excellent overview of various methodologies has been summarized by Randle et. al. [55]. Nevertheless a lack of simple, versatile and cost-effective approaches has contributed to a lack of efforts to quantify the role of this important aspect of grain-boundaries on microstructural evolution and properties. With regard to the concept of CSL, in polycrystalline materials it is not feasible to achieve the conditions of exact coincidence and it has been found that even with some deviation, the properties of such grain-boundaries are close to one expected for an exact CSL. Brandon
et. al. proposed an expression for the allowed deviation ($V_m$) from exact CSL by,

$$V_m = 5\sum^2 \theta [56].$$

Later on it was suggested that instead, $V_m = 5\sum^6 \theta [57]$ gives a better estimate of the deviation. Yet Brandon equation has a wider acceptance in literature. Thus in summary, on a broad scale the concept of misorientation angle/axis has been shown to be useful in understanding the grain-boundary character. Yet, in absence of the orientation of a specific grain boundary plane the exact grain boundary structure cannot be predicted and it imparts a degree of uncertainty on the results described using this approach. In addition, the fact that determining the three-dimensional orientation of a grain-boundary plane is experimentally an expensive problem to solve and it has compounded the issues involved. Thus, there exists a need to develop methods that simply the approach to determine the orientation of an interface.

### 2.9 Evolution of Allotriomorphc α Precipitates

With regard to the nucleation of GBα Kokuz et. al. (2008) reported that these precipitates do not nucleate simultaneously on all grain-boundaries. Instead, a set of following conditions were found for the propensity of the nucleation of allotriomorphs at a given grain-boundary; (a) high misorientation angle (>22°) between prior β grains, (b) The presence of a Burgers orientation relationship with one of the adjacent β grains along with a small deviation from the Burgers-OR with respect to other grain [58]. Further, it was demonstrated that by suitably choosing the heat-treatment conditions, a control over the misorientation distribution can be achieved. In particular, it was shown that as a result
of heating above $\beta$-$\alpha$ transition temperature, the number of high angle grain boundaries between $22^\circ$ and $52.5^\circ$ significantly decreased at high soaking time, while the number of other grain-boundaries did not alter as significantly. The decrease in the fraction of high angle grain boundaries was attributed to high mobility.

A grain-boundary that satisfies the conditions mentioned earlier would be attractive for the nucleation of $\alpha$ precipitates because the energy of $\beta$–$\beta$ boundary is high at high misorientation angles while, as discussed in the previous section, the resultant $\alpha$–$\beta$ interface would have low energy because of the ability to establish an orientation relationship with both grains. This argument can be supported by the observation made in this study that for smaller under-cooling the nucleation of $\alpha$ phase at low angle grain boundaries did not occur even after a long aging time.

The lack of sufficient activation energy at low under-cooling at the low angle grain boundaries probably caused the absence of GB$\alpha$. At higher under-cooling however, as expected, all grain boundaries produced a GB$\alpha$. These observations have also been supported by an independent work done by Kamp et. al. [59]. However, the grain-boundaries where GB$\alpha$ nucleates and conditions mentioned above get satisfied, there are still other regions where no nucleation has taken place, which this work fails to account for. In contrary, a three-dimensional characterization done by Sharma et. al. [60] in a $\beta$-Ti alloy proposed that nucleation probably occurs first at low misorientation angle grain boundaries. However, this suggestion has been inferred from a more developed microstructure and lacks experimental backing and therefore is less reliable. Bhattacharya et. al. [61] has discussed various special cases that produce a near Burgers-OR with both
grains and thus attaining a low-energy configuration. These cases do not consider the orientation of GB plane and solely given an importance to misorientation angle/axis. On the other hand, Furuhashi et. al. [42-43] has put forth stringent conditions on the nucleation of a given allotriomorphic alpha variant on the basis of the orientation of grain-boundary plane, as discussed in the previous section. It was also shown that some deviation from exact Burgers-OR (or Potter-OR) may exist at the grain-boundaries. These also include the cases where none of the grains establish any OR with GB$\alpha$. Considering the observations made in these studies, it becomes clear that preference for the nucleation of $\alpha$ precipitates has two aspects; one is the preference for the of nucleation on certain grain-boundaries that leads to a significant release of $\beta$–$\beta$ interfacial energy and production of low $\alpha$–$\beta$ interfacial energy with respect to both adjacent grains, and second is the selection of that variant of $\alpha$ for which grain boundary plane achieves a stable configuration by orienting close to the habit plane. Thus a combination of GB parameters and Burgers-OR appears to be an important factor in the evolution of GB$\alpha$. It should be reminded at this point that the rules of variant selection [42] are statistical in nature and a deviation in terms of the orientation of the GB plane is possible.

Another conceptual implication of the existing rules of variant selection of GB$\alpha$, which are based on the orientation of the GB plane, is the preference for producing a unique variant at a planar interface. However, observations made on a compositionally graded Ti-8Al-xV alloy [62] confirmed that more than one variant may exist at the same planar grain boundary. This observation could also point towards the possible nucleation of multiple variants of GB$\alpha$ during incipient nucleation events. This study also showed
that the morphology and thickness of GB\(_\alpha\) significantly depend upon the amount of \(\beta\)-stabilizer present in the material. Specifically, when the concentration of V was increased from 1 wt\% to 18 wt\%, the average thickness of GB\(_\alpha\) decreased. Also, it was found that in the \(\alpha+\beta\) regime, the morphology of GB\(_\alpha\) was that of a continuous plate, which progressively converted into discrete circular allotriomorphs (in back-scattered electron images) because of reduced impingement at high concentrations of V. Also a unique case was found wherein GB\(_\alpha\) did not establish an orientation relationship with any of adjacent \(\beta\)-grains. In another study Banerjee et. al. observed a variation in the morphology of this phase with a variation in the curvature of grain boundary plane [63]. A three-dimensional study of the morphology of allotriomorphic \(\alpha\) showed the evolution of branched morphology of precipitates in a \(\beta\)-Ti alloy, which would appear ellipsoidal in a two dimensional image. A detailed discussion on the possible mechanism(s) of the branching of allotriomorphic \(\alpha\) is not available in literature. A similar phenomenon has also been observed for cementite precipitates in steel [64]. Nevertheless, it is interesting to note that the morphological change in these precipitates occurs upon changing the amount of \(\beta\)-stabilizing alloying element.

Step-quench temperature or in other words, under-cooling has a significant role on the growth of GB\(_\alpha\). As discussed earlier, an increase in under-cooling promotes the nucleation of precipitates even in less favorable sites such as low misorientation angle grain boundaries. The average thickness of grain boundary layers of \(\alpha\) decreases at high under-cooling because of a smaller extent of diffusional growth at low temperatures [2]. At a given step quench temperature, the availability of alternate sites for the
heterogeneous nucleation of a phase has a significant effect on precipitation [4]. An example of an average reduction in average thickness at high under-cooling for Ti-64 alloy is given in Figure 23. Here the material was initially β-annealed at 1030°C for 1 hr followed by step-quenched to (1) 900°C @2 hrs and water-quenched, (2) 600°C@2 hrs and water-quenched, (3) 600°C@15 minute and water-quenched, (4) 500°C@15 minutes and water-quenched, and (5) air-cooled to room temperature. Various research works in β-Ti alloys have attributed a significant enhancement in intra-granular precipitation of α to phase-separation reaction, ω precipitates as well as dispersoids, and therefore a corresponding decrease in the extent of grain-boundary precipitation [65-67]. An addition of a small amount of C in Ti-15 (wt%) V-3Sn-3Cr-3Al (Ti-15-3) alloy has been found to significantly increase properties [66]. It has been attributed to the formation of carbides in the grain-interior that affects the microstructural evolution in two ways, (a) it promotes the intra-granular precipitation of a phase leading to a appreciably decreased tendency to produce coarse GBα layer and (b) carbide particles react oxygen to form Ti(CO) complex and thus reduce its chemical segregation at the grain-boundaries. A later work on this system has proposed the formation of vacancy-carbon-oxygen complex in the solid solution as the main factor that limits the chemical segregation of oxygen at grain-boundaries [67]. Thus these studies also emphasize the role of chemical segregation on the growth of GBα.

In Summary the following facts about the evolution of GBα are important to consider:
Different experiments have shown that the variant selection occurring at grain-boundary is influenced either by grain-boundary plane or misorientation angle/axis only. On the contrary both these factors equally influence the variant selection. Hence there is a need to evaluate the role of all GB parameters simultaneously to isolate their relative importance.

The factors that affect the morphology and thickness of GBα are,

- Cooling rate from the β to α transition temperature where fast cooling leads to a reduction in average thickness
- Chemical composition of alloy: high β-stability leads to a reduction in average thickness and produces a discrete morphology
- Chemical segregation at the grain-boundaries: Segregation of oxygen etc promotes the formation of GBα
- Grain-boundary parameters: early nucleation at high angle grain-boundaries
- Variant selection

In literature the role of thermo-mechanical processing, chemical composition, grain-boundary segregation etc. have been accessed to evaluate the average response of allotriomorphic α. However, there exists an urgent need to isolate the local response of the precipitation and morphological evolution of these precipitates caused by the variant selection and grain-boundary parameters. Such an example is shown in Figure 23, where is observed that the thickness and the morphologies of GBα are significantly distinct (continuous, blocky, thick and thin) at different grain-boundaries. Such a work is important because it would help to understand the
parameters that govern the variability in the evolution of this phase at different grain-boundaries under the same external conditions.

2.10 Effect of the Evolution of GBα on the Intra-Granular α Precipitation

With regard to the evolution of microstructural evolution in the grain interior, during the early growth stages, it is hypothesized that the morphology of GBα could influence the early nucleation of Widmanstätten α plates. Such as example is from the observations made in the present work is shown in Figure 24, where evidently an early formation of Widmanstätten α plates occurs close to the blocky GBα; while, it is not present close to relatively continuous precipitates. In the fully developed microstructure, an EBSD study done on Ti-550 alloy by Lee et. al. [68] showed that for the given heat-treatment the formation of colony microstructure is preferred on the ‘Burgers’ side. As expected, Widmanstätten side plates of α keep the same crystallographic orientation as that of GB α in this region. However, different variants of α were found to present on the ‘non-Burgers’ side, leading to the appearance of a basketweave microstructure. The self-accommodation of strain energy caused by the phase transformation (bcc to hcp) was used to explain the formation of basket weave microstructure on the basis of works done by Wen. et. al. for coupled diffusive-displacive phase transformations [69-70] and Christian et. al. [71] for the cases where a cluster consisted of three variants of α sharing a common \([1 \overline{1} 1 \overline{1} \parallel [0 0 0 1]_\alpha\) direction, with individual [0001] pole rotated with respect to one other by 60°. However, this explanation can be used to rationalize the presence of
basketweave microstructure in general and thus it does not elucidate the contribution of GBα on the exact variant selection (if any) or morphology of α precipitates on the ‘non-Burgers’ side. Also, the presence of another type of clusters namely, two α sharing a common (0001) plane and individual \([1 \bar{T} 1]_α \parallel [1 1 2 0]_α\) directions getting rotated by 10.5° has not been not explained and requires further investigation. This particular orientation relationship in two neighboring colonies has been also been reported by Bhattacharyya et. al. in β processed Ti-6Al-2Sn-4Zr-6Mo alloy, and its role on the development of spatial morphology of colony microstructure has been discussed [72]. In another work, Bhattacharyya et. al. showed that for a special case where (0001) of α phase is parallel to common (110) plane of adjacent β grains, it establishes a Burgers OR with both grains. In such cases, the growth directions of side plates get inclined by ~89°. Again if β grains maintain a twin relationship, again a Burgers OR is produced with both grains and in this case, growth directions get rotated by ~28.8° [61].

These studies suggest a larger degree of contribution of variant selection on the microstructural evolution, which possibly exceed much beyond its role on the evolution of allotriomorphic α precipitates in titanium alloys and it contributes to the presence of transformation texture. Once orientation relationships as well as other grain boundary properties decide the characteristics of GBα, a further control may be exercised on the crystallography and morphology of adjacent intra-granular α precipitates depending upon the kind of interaction GBα has with neighboring β grains. Especially in case of a β processed microstructure where material is slow-cooled, there is a smaller degree of
intra-granular precipitation of $\alpha$ plates. In such cases, there is a relatively high fraction of Widmanstätten $\alpha$ colonies adjacent to GB$\alpha$ and transformation textures become an important factor. As an example, in an EBSD study of a $\beta$-processed Ti-6Al-4V alloy, it was found that instead of producing all twelve variant with equal probability in the grain-interior, the overall texture of the material showed to have a preference for certain variants of $\alpha$ [44]. In a recent work, it has also been established that the degree of nucleation of side plate at a grain boundary is higher at higher misorientation angles [73]. Further, a clear preference for the nucleation of a precipitates satisfying the selection criteria suggested by Bhattacharyya et. al [72] was observed and variant selection was proposed to be the primary factor governing the microstructure and texture evolution for the studied alloy systems.

2.11 Influence of Allotriomorphic $\alpha$ on Mechanical Properties

A microstructure-mechanical properties chart developed by Lütjering et. al.[Table 1] has qualitatively summarized the negative influence of GB$\alpha$ layers on three properties namely, ductility, high cycle fatigue (HCF) [3] and fracture toughness [2].

This effect depends mainly upon the relative strength between microstructure in grain-interior as compared to that at the grain boundary. In case of $\alpha+\beta$ alloys, this difference is not significantly large for the colony microstructure. However on increasing the cooling rate, the refinement of intra-granular precipitates occur (a basketweave morphology) and consequently the relative strength increases. The strength differential
causes the localized deformation at the grain-boundary that directly influences the ductility of the material [1]. On increasing the amount of \( \beta \) stabilizers, a finer precipitation of \( \alpha \) phase in the matrix can be achieved and contributes to a higher strength differential. Also in these alloys, the formation of grain boundary precipitates contributes to the formation of surrounding denuded zone, which is significantly softer. It drastically reduced the ductility of \( \beta \)-Titanium alloys. It does not affect yield stress values because of its low volume fraction. Figure 25 shows the localized deformation at the grain boundary and also HCF crack nucleation and growth along continuous GB\( \alpha \).

Table 2: Table summarizes qualitatively the influence of various microstructural features on mechanical properties in titanium alloys. GB\( \alpha \) generally has a negative influence on various properties.

<table>
<thead>
<tr>
<th>( \alpha + \beta ) Titanium Alloys</th>
<th>( \sigma_y )</th>
<th>( \sigma_f )</th>
<th>HCF</th>
<th>Microcracks ( da/dN )</th>
<th>Macrocracks ( \Delta K_{th} ) ( R=0.7 )</th>
<th>( K_{IC} )</th>
<th>( \Delta K_{th} ) ( R=0.1 )</th>
<th>Creep Strength ( 0.2% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging (( \alpha_2 )) Oxygen</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Bi-modal Structure</td>
<td>+</td>
<td>+</td>
<td>-/+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GB ( \alpha ) Layers</td>
<td>( \theta )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( \theta )</td>
<td>-</td>
<td>( \theta )</td>
<td>( \theta )</td>
</tr>
<tr>
<td>Small ( \alpha )-Colonies ( \alpha )-Lamellae</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The nucleation of a material during HCF occurs preferably along continuous GB \( \alpha \) layers in a \( \beta \)-annealed microstructure or at the largest intra-granular \( \alpha \) precipitates in

32
the $\alpha+\beta$ processed condition. In both cases of tensile as well as fatigue failure, experimental investigations found the propensity for nucleation of crack at triple points and its growth along the $\alpha-\beta$ interface of GB$\alpha$ and $\beta$ matrix [3,74]. Therefore various works have suggested using thermo-mechanical treatments (e.g. $\beta$ or $\alpha+\beta$ processing) to produce broken-up GB $\alpha$ [58]. The presence of GB $\alpha$ cannot be avoided in these heat-treatments. On the other hand, certain alloying additions (such as carbon) have been found to nearly eliminate the formation of these precipitates. Consequently, a drastic increase in ductility of high strength $\beta$-Ti alloys has been reported [66].

### 2.12 Summary

Various research efforts in last three or four decades have contributed to an enhanced understanding of the evolution of allotriomorphic $\alpha$ in titanium alloys and important factors have been evaluated to a certain extent. However, there still exist a number of key issues that need to be addressed. These are:

- The formation of allotriomorphic $\alpha$ involves a variant selection in a bid to minimize the energy requirements for the nucleation and subsequent diffusional growth. It has been suggested in various studies that both misorientation angle/axis as well as grain-boundary plane have an important role. However, a comprehensive attempt to evaluate and compare their contributions is required. Also, the existing selection criteria predict the preference for a unique variant at a
planar interface. Therefore, the presence of multiple variants in certain cases needs an explanation.

- Despite being highlighted as one of the key parameters for the evolution various grain-boundary related phenomenon, the quantification of the role of crystallographic orientation and curvature of grain boundary plane has not been done in most of the studies. The main reason is the lack of simple and cost-effective methods to determine its orientation.

- The contribution of GB parameters on the morphology of GBα as well as the interfacial structure between GBα and β has not been experimentally addressed in literature.
Figures

Figure 1: Schematics show the crystal structures of, (a) β phase at 900°C and (b) α phase [1].
Figure 2: Plot shows the anisotropic elastic behavior of $\alpha$ phase for different declination angles [1].
Figure 3: Schematic shows important slip planes and slip directions present in hcp $\alpha$ phase in titanium alloys [1].

Figure 4: Schematics show the effect of different alloying additions on the phase stability of $\alpha$ and $\beta$ phases [1].
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Figure 9: Micrographs show the early nucleation of $\alpha$ phase at the grain-boundaries in Ti-5553, which then proceeds to grain-interior [Welk et.al., unpublished work].
Figure 10: Micrographs show the development of (a) colony microstructure and (b) basketweave microstructure for slow and fast cooling rates from the β-phase field during β-processing.
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Figure 12: Texture evolution in during β-processing in Ti-17 alloy, produced using neutron-diffraction [16].

Figure 13: The interfacial energies of β-β and α-β interfaces in both adjacent grains determine the optimum shape of allotriomorphic precipitates.
Figure 14: Inverse pole figures show a deviation from the exact Burgers-OR between GB_α and (a) β-grain that produced an orientation relationship and (b) β-grain that did not establish an orientation relationship.
Figure 15: Schematic shows Burgers-OR in titanium alloys.
Figure 16: Schematic shows the interfacial structure of Widmanstätten $\alpha$ and $\beta$ phase [29].
Figure 17: polar plot shows the minimum energy configuration along the broad face or habit plane for a Burgers-OR between $\alpha$ and $\beta$ phases in titanium alloys [32].
Figure 18: Plot shows the preference of the selected variant to orient the grain-boundary plane nearly normal to [111][11-20] of Burgers-OR [Furuhara et.al.(1991)].

Figure 19: Pole figures show an example of the selection of crystallographic variant of GB$\alpha$, which is controlled by the close [101] poles. This variant also gets adopted by the adjacent Widmanstätten $\alpha$ plates on the "Burgers’ grain [44].
Figure 20: Schematics show (a) the geometry of a low angle grain-boundary by the means of dislocation model and (b) an increase in its energy at higher misorientation angles until it eventually saturates at high misorientation angles [4].

Figure 21: At high misorientation angles, for certain geometrical configurations the interfacial energy of a grain-boundary achieves a minima corresponding to the coincidence site lattice [4].
Figure 22: Micrographs (i)-(iv) and corresponding plot show a decrease in the average thickness of allotriomorphs in Ti-64 alloy at higher under-cooling temperature (1): 900°C, (2-3): 600°C for 2 hrs and 15 min, (4): 500°C for 15 min and (5) air-cool to room temperature [Dixit. et. al. (unpublished work)].
Figure 23: Micrographs show a variation in morphological response of GBα.
Figure 24: Micrograph shows a variation in the early formation of Widmanstätten $\alpha$ corresponding to ‘continuous’ or ‘blocky’ morphologies of GB$\alpha$.

Figure 25: Micrographs show examples of cases where GB$\alpha$ negatively influences various mechanical properties: (a) localized grain-boundary deformation [1], (b) high cycle fatigue crack nucleation [58] and (c) crack growth respectively [3].
Chapter 3
Experimental Procedures and Initial Characterization

3.1 Abstract

In order to develop a better understanding of the both crystallography and morphology of grain-boundary $\alpha$ (GB$\alpha$) in titanium alloys, suitable alloy systems and correspondingly adequate heat-treatments need to be utilized to capture different stages of the evolution of these allotriomorphs. More importantly, different characterization tools have to be used to evaluate their evolution at these different stages. Traditionally, transmission electron microscopy (TEM) has been used, which has proven useful in providing answers to certain aspects. Unfortunately, the time-consuming and expensive sample-preparation methodology in this approach has contributed to a lack of statistics. On the other hand, this technique is indispensable in determining the interfacial defect-structure between GB$\alpha$ and $\beta$. In this chapter, in addition to thermal treatments that have been performed on Ti-5553 and Ti-550, novel characterization techniques e.g. dual beam focused ion beam (FIB) and electron back-scattered diffraction (EBSD) have been discussed that have been used to correlate crystallography and morphology at sub-micrometer to micrometer size-scale. Finally, the TEM based approach to understand the interfacial structure of GB$\alpha$-$\beta$ interfaces at certain grain-boundaries has been discussed.
3.2 Introduction

Traditionally, quantification of the role of grain-boundary parameters on the morphology and variant selection of allotriomorphic $\alpha$ in titanium alloys have been carried out using transmission electron microscopy (TEM), which is experimentally a time intensive and expensive approach. This approach is indispensable to study the nucleation and early growth stages of this phase. But, depending upon the chemical composition of the material and the thermal treatment, the size-scale of these features could approach sub-micrometers to micro-meters in a more developed microstructure. In these cases, scanning electron microscopy based techniques such as, focused ion beam (FIB) and electron back-scattered diffraction (EBSD) become more useful. These techniques have significantly simpler and cost-effective sample preparation requirements. More importantly, a three-dimensional characterization of a large number of interfacial precipitates can be performed relatively quickly by using a combination of these tools.

In this chapter, a brief description of materials systems: Ti-550 and Ti-5553 and the thermal treatments used to capture various stages of the evolution of GB$\alpha$ will be given. Ti-550 is a $\alpha/\beta$- and Ti-5553 is $\beta$-titanium alloy system. These alloys have been chosen because of their extensive usage in a variety of commercial and strategic applications as well as their ease of characterization, especially at sub-micron scale in slow cooled microstructures. Subsequently, various electron microscopy based characterization techniques used in the present work, namely, scanning electron microscopy (SEM), dual beam FIB, EBSD, TEM and electron dispersive spectroscopy (EDS) have been described.
3.3 Materials Systems and Heat-Treatments

The materials systems used to study the evolution of GBα in the present work are Ti-550 alloy and Ti-5553 alloy. The chemical composition of Ti-550 alloy is: Ti–4 (wt %) Al–4Mo–2Sn–0.5Si and the chemical composition of Ti-5553 is: Ti-5Al-5Mo-5V-3Cr. Ti-550 is an α/β alloy system, while Ti-5553 is a β-alloy. The rationale for choosing Ti-550 over other α/β systems such as Ti-5Al-1V-1Zr-1Sn (Ti-5111) or Ti-6Al-4V (Ti-64) is the relative ease with which its microstructure can be analyzed using secondary electron imaging mode in SEM or FIB. Figure 26 shows the secondary electron images for Ti-550 and Ti-5553 alloys respectively, taken from FEI-Helios microscope. Evidently it became progressively easier to delineate α and β phases even in the secondary electron imaging mode at higher β-stability in Helios FIB microscope. Also, Ti-5553 does not undergo a martensitic transformation upon quenching to room temperature from a temperature above the β–α transition temperature (~850°C), and retains the β-phase. Upon quenching, it produces nanometer size ω phase precipitates [75], but the size scale of these features remains below the resolution limit of EBSD and does not interfere with the crystallographic data collected. Thus such an alloy is experimentally an easier system to study the early growth stages of the evolution of allotriomorphic α and relate with the parent phase. Ti-550 alloy on the other hand, undergoes a martensitic transformation upon water quenching (Figure 27). The details of the various heat-treatments for each of the alloy systems used in the present study are described in the next section.
3.3.1 Ti-550 Alloy: Thermal Treatments

The as received forged material was sectioned into a small section (10mm x 10mm x 50 mm) and was heated at 1020°C (β-α transition temperature~925°C) in the conventional drop-furnace for 1.5 hours. A flow of inert gas was maintained in the chamber to minimize the extent of oxygen-ingress. In addition, the sample was covered with titanium sponge and wrapped in a titanium foil to getter oxygen. Subsequently, material was cooled in the furnace to room temperature (Figure 28a).

Another set of controlled heat-treatment was performed using the electro thermo-mechanical tester (ETMT) with an aim to capture the early stages of the formation of GBα. Here, samples were sections in the formed of rectangular bars (2 mm x 2 mm x 20 mm) and polished to remove the oxide layer. These samples were initially heated at 1020°C for 30 min and were step-quenched to 910°C-930°C and soaked for 1 hour in an inert atmosphere. Finally these samples were water-quenched. A schematic of these heat-treatments is shown Figure 28b.

3.3.2 Ti-5553 Alloy: Thermal Treatments

In order to capture the early growth stages of the evolution of GBα, Ti-5553 was subjected to various thermal treatments. The β to α transition temperature is close to 850°C. Therefore, material was initially heated at 1000°C for 15 minutes using a conventional tube furnace. Again, a flow of Argon was maintained to minimize the
ingress of oxygen. Samples were wrapped in titanium foil to further reduce the possibility of oxygen ingress. Subsequently, samples were cooled to 825°C, 800°C, 775°C and 750°C respectively at the cooling rate of 5°C/min. Finally samples were water quenched to room temperature to arrest the formation of α phase and retain β-phase in the matrix (Figure 29a).

Another set of experiment that was performed on this material was to initially β-anneal the sample at 1000°C for 15 minutes. Afterwards it was water quenched and again heated at the rate of 5°C/min and soaked at 650°C for 2 hours. Finally, the sample was water-quenched (Figure 29b).

For subsequent characterization, all specimens were sectioned in the middle and the exposed surface was subjected to mechanical polishing using standard metallographic techniques. In the final step, material was kept in a vibratory polisher in the suspension of 0.05 μm silica particles for a number of hours to achieve a mirror-finish.

3.4 Characterization Techniques

Figure 30 shows different kinds of signals that are generated as a result of an interaction of a high energy electron beam with a crystalline solid matter [76]. Signals such as characteristic x-rays as well as inelastically scattered electrons are used for the analysis of chemistry using XEDS (x-ray energy-dispersive spectroscopy) and EELS (electron energy-loss spectroscopy). Back-scattered electrons as well as secondary electrons are not used in transmission electron microscopy (TEM) but are inherent
aspects of scanning electron microscopy (SEM). Elastically scattered electrons are present in the form of diffracted beam as well as direct beam, and constitute the main modes for studies in TEM and EBSD. These signals are extremely useful in the analysis of spatial and crystallographic relationships of various microstructural features, including various phases as well as defects. A brief description of important advanced electron microscopy based techniques that have been utilized this work to analyze allotriomorphic phase transformations in titanium alloys is given below.

3.4.1 Scanning Electron Microscope

Two scanning electron microscopes have been used in the present work. For the high resolution secondary electron (SE) and back-scattered electron (BSE) imaging, FEI Sirion™ microscope has been used. This system is also equipped with the “Through the Lens Detector (TLD)” for the high resolution imaging in the secondary electron imaging mode as well as Energy Dispersive Spectrometer (EDS) for the chemical analysis of various phases. In general, the operating voltage of 10 kV, spot-size 4 and working distance of 4 mm has been used for acquiring images on this microscope.

The electron back-scattered detector loaded on FEI ESEM™ system has been used to obtain and analyze the crystallographic orientation maps and data of various crystalline phases in the material. The operating conditions used to acquire crystallographic data were: voltage-25 kV, spot-size-4, working distance-20 mm.
This system has also been used to qualitatively determine the chemical segregation of various species between \( \alpha \) and \( \beta \) phases in micron-size precipitates by using the electron-dispersive spectroscopy (EDS).

3.4.2 Electron Back-Scattered Diffraction (EBSD)

The crystallographic studies at sub-micron (and larger) size scale can be performed using EBSD. It uses the diffraction of elastically scattered back-scattered electron in SEM (Bragg’s law). The fraction of such electron emitted out of the surface of the specimen increases at higher inclination with respect to the electron beam and is given by [77],

\[
\frac{\eta_{\text{BSE}}}{\eta_{\text{int}}} = \sqrt{1 + \cos \theta}.
\]

Thus back-scattered electron can be used in two ways. Firstly, it responds to the average atomic number of the phase and thus can be used to differentiate and image different phases (that have different concentrations of atomic species). The second application of it is to determine the crystallographic orientations of crystals of different phases. For the imaging, sample is needed to bring close to the detector to increase the collection-efficiency. While, for the crystallographic data-collection, EBSD detector is installed at 70\(^\circ\) with respect to the electron beam and sample is tilted to align its surface-normal towards the EBSD detector. A high degree of accuracy of the alignment of the sample relative to the detector is needed. An error caused by the relative geometric
misalignment gets exponentially propagated to the errors in the data collected and distortion of microstructural features in the inverse pole figure (IPF) map.

In the present work, the accuracy of the data collection has been evaluated using a single crystal of silicon. The surface of this sample was oriented towards <100> direction. The resulting pole-figure is shown in Figure 31, which shows that one of the <100> poles nearly at the center of the plot and confirms the reliability of the setup.

In this method, Kikuchi patterns get produced. These patterns in EBSD are similar to one observed in transmission electron microscopy, are caused by dynamical or multiple scattering [76]. With reference to Figure 30, the interaction of electrons with solid matter results in both elastic and inelastic scattering. Within elastic scattering, the resulting scattering can be coherent or incoherent. The generation of Kikuchi pattern is an example of coherent dynamical scattering. One example of a Kikuchi pattern is shown in Figure 32 [78]. The intersection of various Kikuchi band forms a crystallographic zone. The spacing of Kikuchi bands and their spatial orientation in the detector contain both crystallographic information as well as the orientation of sample relative to some spatial reference frame. In the present work, OIM-TSL software has been used to analyze the patterns, which uses Hough transform to solve them. This approach essentially transforms each band to a single point in the Hough space, and significantly makes the identification easier. The reliability of solution is accessed by confidence index (CI), where relies on the voting system to compare different possible solutions [79-80]. More importantly, this automated approach eliminates user interaction/ judgment and makes the data generation and analysis significantly faster.
In general, the collected data is produced in the form of color-coded inverse pole figure (IPF) map. An example of such a map is shown in Figure 33 for a hot rolled plate of Al-2024 alloy [81]. The color-coding of these different orientations is done according to the orientation of z-axis of the sample reference frame. Thus, care needs to be exercise while making interpretations just on the basis of the color of the IPF maps. The reference color-scheme for IPF maps for cubic and hexagonal crystals is shown in Figure 34.

In this work, the data collection and analysis of the orientation of various grains is in terms of Euler angles in the convention developed by Bunge et. al. [82-83]. Euler angles essentially relate two different reference frames. There also exist other formats that can be used to relate different reference frames e.g. quaternion, angle/axis, orientation matrix etc. Data can be easily converted among these formats using the equations that related them. The details of relationships between these different formats are described elsewhere [84]. In this study, primarily Euler angles, orientation matrix and Quaternion formats have been used to represent the orientation of a grain with respect to the reference frame of the EBSD and perform mathematical calculations. The definition of the EBSD reference frame with respect to the geometrical orientation a sample in the SEM chamber is shown in Figure 34 [85].

In the present work, suitable step-size for the data-collection was decided by the size of the features of interest. For Ti-5553, a step size of ~ 0.5 mm was used while for Ti-550, the step-size was kept at 1.7 μm.

This technique is particularly useful in studying the crystallographic relationships and deformation characteristics on a (sub) micrometer scale with significantly better
statistics. When combined with dual beam focused ion-beam, it offers a distinct advantage over the TEM technique with respect to correlating morphology with crystallography even for large microstructural features. In addition, the requirements of sample preparations are significantly simpler in this approach. In this work, owing the advantages offered in this technique a large number of allotriomorphic precipitates have been analyzed. On the other hand, this technique suffers from the lack of accuracy in comparison to TEM, and cannot be used to probe the local microstructural details at higher magnifications.

3.4.3 Focused Ion Beam (FIB)

In this study, an FEI Helios™ DualBeam™ focused ion beam (FIB) has been a major characterization tool and has been used to expose the three-dimensional orientations of grain-boundaries as well as the morphology of allotriomorphic α phase and Widmanstätten α plates in titanium alloys. FIB is a micro-machining and microscopy tool that uses a liquid metal ion source, consisting Gallium metal to mill the region of interest at a rate and resolution, which is decided by the accelerating voltage and aperture diameter. Gallium metal wets the Tungsten tip, which upon the application of electric-field emits Ga ions. Electromagnetic lenses are used to focus this ion-beam onto the sample. The secondary electron beam source is oriented at 52° with respect to the ion-beam source (Figure 36). The details of the setup, advantages and issues associated with techniques have been described in detail elsewhere [86]. In this study the imaging of the sectioned surface was performed primarily using the electron beam. In some isolated
cases, the sample was rotated to the tilt of 0°. In this case, the sample surface normal made an angle of 52° with the ion beam, which was then used to image the sectioned region.

This approach was also used to produce site-specific TEM foils. As shown in Figure 37, a FIB trench was produced on the both sides of the region of interest and an undercut is produced on three sides. In the next step, an Omni-probe was inserted at the sample tilt of 0°, and is welded with the sample. Finally thin-foil was welded to the Omni-grid. As shown in Figure 38, further sample-thinning was performed to achieve an electron transparency. The reduction in the thickness is generally monitored by a variation in the contrast observed during the thinning process.

3.4.4 Transmission Electron Microscope

A majority of investigations regarding the crystallography of different phases and the defect analysis of the interfacial structure between GBα and β matrix have been performed on FEI/Phillips CM200T transmission electron microscope. This microscope has a thermionic LaB$_6$ filament and the allowed goniometer tilts of, alpha $\sim \pm 55^\circ$ and beta $\sim \pm 30^\circ$.

The microscope is also equipped with an “Ultra Thin Window” EDS detector to perform chemical analysis. The operating conditions used for the analysis are: voltage-200 kV, working distance-500mm.
The chemical analysis of $\alpha$ and $\beta$ phases has been carried out on FEI (S)TEM Tecnai™ TF20T microscope in the scanning transmission electron microscopy (STEM) mode. The working distance was kept generally at 330 mm and gun-lens 3 and spot-size 4 were used. The EDS system is equipped with ultrathin window (Si-Li) detector and is suitable for the reliable analysis of elements that have medium to high atomic numbers. A details description of the setup as well as instrumentation of the system is described elsewhere [87].

The analysis of defect-structure between GB$\alpha$ and $\beta$ phases is more complicated than defects present in the grain-interior. An interface connects two grains and therefore their response to electron beam has been found to be different than matrix-dislocations because of the elastic anisotropy of adjacent crystals. Details of these differences and their implications have been described elsewhere [88]. The analysis of defects can be performed in three-different modes: (a) a two beam condition only with respect to one of the grains, (b) two-beam conditions with respect to both grains with same diffraction vectors and (c) two-beam conditions with respect to both grains with different ‘$g$’ vectors [89]. In the present work, mode (a) of producing a two-beam condition with respect to only one phase (GB$\alpha$) has been used in most of the cases.
3.5 Initial Characterization of Alloy Systems

3.5.1 Ti-550 Alloy

β-processing of Ti-550 alloy produced a colony microstructure in the material. A progression of the microstructural evolution for (a) step-quenched to 915°C and soaked for 1 hr after β-annealing and finally water-quenched (b) furnace cooled microstructure is shown in Figure 39. With respect to the microstructural evolution in Ti-5553 [3, 90], Ti-550 alloy appears to exhibit a similar precipitation response. Evidently, an anisotropic precipitation of GBα occurs at different grain-boundaries. In the fully-developed microstructure in the furnace cooled sample, colony microstructure evolution. As expected, a significant reduction in the amount of b-phase is observed in this a/b-alloy system. This diffusional phase transformation results in a chemical segregation of various solute atoms. The precipitated phase rejects transition elements such as Mo and enriches in Al in this process (Figure 40 and Figure 41). Sn and Zr did not exhibit any preference towards any of the phases and remained neutral.

3.5.2 Ti-5553 Alloy

The as-received sample of Ti-5553 alloy consisted of globular α because of α+β processing (Figure 43); details are provided elsewhere [4]. The material for this work came from the same lot used by Foltz et. al. (2010) and Welk et. al.(2010).

The compositional segregation of different solute atoms is shown in Figure 44, where transition elements Mo, Cr, Fe etc. segregate towards β-phase and Al segregates...
towards $\alpha$. Detailed analysis of microstructural evolution involving morphology and
 crystallography will be done later in chapter-6 of this document.

3.6 Summary

In this work, both crystallographic and morphological aspects of allotriomorphic
$\alpha$ in $\beta$-processed Ti-550 and Ti-5553 alloys have been studied. At a micrometer scale,
correlations between morphology and crystallography have been captured using a novel
combination of dual beam FIB, SEM and EBSD. Also, interfacial defect-structure
between GB$\alpha$ and $\beta$ phases has been studied using a conventional TEM.

The initial characterization and chemical analysis using (S) TEM-EDS of both
alloys reveal development of similar microstructural features, especially for a small
under-cooling temperature in Ti-550. As expected, chemical segregation of solute atoms
occurs during this diffusional transformation where, transition elements: Mo, Cr, Fe etc
segregate towards $\beta$-phase and Al segregate towards $\alpha$-phase. Sn and Zr remain neutral
to the phase transformation.
Figures

Figure 26: Micrographs show a difference in contrast between $\alpha$ and $\beta$ phases, and therefore an ease of analysis using secondary electron imaging in Helios microscope for (a) Ti-550 and (b) Ti-5553.
Figure 27: Micrograph shows the production of Martensite in a β-annealed and water-quenched sample of Ti-550 alloy.
Figure 28: Schematic shows the set of heat-treatments performed on Ti-550 alloy.

Figure 29: Schematic shows the set of heat-treatments performed on Ti-5553 alloy.
Figure 30: Schematic shows the generation of different kinds of signals upon the interaction of a material with electron-beam.
Figure 31: Pole figure shows the orientation of the $<$100$>$ poles of silicon wafer. The closeness of the pole to the center of the pole confirms the reliability of the EBSD data collection.
Figure 32: Micrographs shows an example of Kikuchi pattern produced during the EBSD data collection of Ti-64 alloy [78].
Figure 33: Micrograph shows the crystallographic orientations of β-grains in Ti-5553 alloy.

Figure 34: Figures show the color-scheme of IPF maps according to the crystallographic orientation of sample normal in EBSD for (a) cubic and (b) hexagonal samples.
Figure 35: Schematic shows the orientation of EBSD reference frame relative to the sample surface in the SEM chamber, as defined in OIM-TSL software [85].
Figure 36: Schematic shows the configuration of ion-beam and electron-beam in a FIB-chamber.
Figure 37: Micrographs show various steps involved in producing a site-specific TEM foil using FIB.

Figure 38: Micrograph shows a change in contrast with sample thickness during thinning.
Figure 39: Micrographs shows the microstructure of Ti-550 alloy subjected to β-annealing at 1020°C followed by, (a) step quenching to 915°C and water-quenching and (b) furnace-cooling to room temperature.
Figure 40: Composition maps show a significant rejection of Mo from $\alpha$ phase and an accumulation of Al in it during $\beta$-$\alpha$ phase transformation in Ti-550 at 915°C.
Figure 41: Composition profile collected using (S) TEM-EDS across GBα and β matrix in Ti-550 alloy show a segregation of Mo towards β. Sn remains relatively neutral and Al prefer to segregate towards α phase.
Figure 42: Micrograph shows the microstructure of as-received material of Ti-5553 alloys [3].
Figure 43: Micrographs show a progression of microstructural evolution in Ti-5553 alloy upon a decrease in under-cooling temperature of (a) 825°C, (b) 800°C, (c) 750°C and (d) 700°C.
Figure 44: Composition profile shows a significant rejection of Mo, Cr, Fe and V from $\alpha$ phase and an accumulation of Al in it during $\beta$-$\alpha$ phase transformation in Ti-5553 at for the microstructure shown in Figure 43b.
Chapter 4  
Methods to Determine Local Crystallographic Orientation of a Grain-Boundary Plane

4.1 Abstract

A complete description of grain-boundary (GB) parameters involves quantification of both the misorientation angle/axis and the GB plane. In contrary to misorientation angle/axis, it has proven difficult to determine the crystallographic orientation of a GB plane relative to adjacent grains because of its three-dimensional nature. In the present work, two simple and versatile methods have been proposed. Both methods utilize a combination of scanning electron microscopy (SEM), electron back-scattered diffraction (EBSD) and dual-beam focused ion beam (FIB). The accuracy of these methods has been validated and analyzed using the knowledge of crystallographic characteristics of twins present in both cubic and hexagonal systems.

4.2 Introduction

In polycrystalline materials systems, the importance of grain-boundaries is well known. These locations are preferred sites for the heterogeneous precipitation of second phase [4]. Various studies have shown their effect on the crystallography and morphology of allotriomorphic precipitates [5, 11, 90] as well as on various mechanical properties [1, 3]. Therefore it becomes imperative to completely characterize these
inherent features in polycrystalline materials. A complete macroscopic description of a
grain-boundary (GB) consists of the following parameters, (a) misorientation angle, (b)misorientation axis and (c) orientation of GB plane. In Thus, determination of five
parameters is needed for a complete description of grain-boundaries.

Interestingly, only a small fraction of overall literature concerning grain-boundaries has actually quantified the contribution of GB plane [92]. The primary reason
for this trend has been a lack of simple and cost-effective methods to determine the
crystallographic orientation relative to adjacent phases of this three-dimensional
geometrical aspect. Misorientation angle/ axis are related to the crystallographic
symmetries of the neighboring grains. Thus, these aspects can be quantified relatively
easily using x-ray and electron microscopy based diffraction experiments. This ease of
quantification is demonstrated by a number of reports concerning their influence on
microstructure and properties [3].

In an attempt to measure the orientation of a GB plane, a number of methods have
been developed mainly in last three decades that utilize either scanning electron
microscopy (SEM) or transmission electron microscopy (TEM) [5-7]. In almost all of
these studies, different representations of a two-surface trace analysis have been used.
Two-surface trace analysis is essentially finding the crystallographic orientation of two
non-collinear lines lying on the surface of the interface. A vector product of these
directions then gives the desired orientation of the interface. A brief description of each
of these techniques follows.
4.2.1 Existing Methods to Determine Crystallographic Orientation of an Interface

**TEM Based Techniques**

In TEM based techniques, a sample is tilted either to bring the interface edge-on relative to the beam, or in other words, to get minimum thickness relative to the precipitate [42, 90]. The corresponding tilt angles are recorded relative to the closet major-zones to determine its crystallographic orientation. For special boundaries, the crystallographic symmetries of adjacent grains have been used to determine the orientation of the interface [51]. Another approach is to determine two vectors lying on the interface and then perform their cross-products to determine the orientation of the given interfacial plane, which is essentially an extension of determining the line directions of non-collinear interfacial defects [93]. This exercise can be performed either mathematically or by using stereographic projection. An example of this approach will be discussed in chapter-5 of this document. The major advantage of this method is that it gives an opportunity to evaluate in detail the interfacial structure of the grain-boundary plane. Unfortunately, the preparation of a TEM foil is relatively expensive and a time-intensive endeavor, which makes acquiring data from a large number of interfaces rather difficult. Thus, this approach is more likely to result in a lack of statistical reliability.

**SEM/Optical Microscopy Based Techniques**

Sample preparation requirements are significantly simplified by using SEM (combined EBSD and electron imaging) based techniques. A significantly large number of boundaries can be analyzed with relatively less efforts resulting in appreciably better
statistics. Both two-dimensional and three-dimensional approaches have been developed. Two dimensional methods are extremely successful in predicting the inclination of special boundaries, such as twins [94]. More recently, complicated sub-routines based on EBSD and stereology have evolved to predict complete grain-boundary character from two-dimensional data on a statistical basis [95]. Such approaches have significantly reduced the requirement of expensive experiments and enhanced the understanding of the influence of GB parameters on average properties.

The local orientation of a GB plane at a given grain-boundary can be calculated using the three-dimensional techniques. Thus far, two main approaches have been adopted. One approach is based on parallel serial-sectioning of samples using either conventional metallography or FIB [11, 53-54]. The depth of sectioning has been measured using indentation marks. Then, the lateral movement in the interface trace after a certain depth is measured to determine its inclination relative to the polished surface [96]. Individual slices can then be stacked up and a three-dimensional microstructure can be produced [54]. An example of this approach is shown in Figure 45 for a titanium alloy, where a superimposed image of a section after successive polishing steps is produced. These stacks of successive images can also be used to reproduce the actual three-dimensional microstructure (Figure 46). In another approach, the specimen is polished along two different orientations to expose an interface on two different surfaces [97] (Figure 47). The orientation of a GB plane can then be determined using the cross-product of the directions along two traces of the exposed interface. An excellent overview of all these methods has been summarized else where [55].

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4.2.2 Issues with Current SEM/Optical Microscopy Based Approaches

Existing three-dimensional methods based on parallel serial-sectioning and reconstruction involve tedious data analysis procedures and/or experimental requirements. Moreover, some of these difficulties can lead to inaccuracies. One major problem in this method is the relative movement of the imaged locations as well as variations in the depth of material removal between consecutive slices [96]. Also traditionally, indentation marks have been used for the manual/automatic alignment. The diminishing area of indents with each slice, indistinct boundary between deformed and pristine regions, and anisotropic deformation could introduce significant errors in characterizing fine features in textured microstructures, such as $\alpha/\beta$-titanium alloys. One example of the anisotropic deformed area produced by a Vickers indent in a $\beta$-processed titanium alloy is shown in Figure 48a; it is clear that this anisotropy diminishes the reliability of a depth measurement. In contrast, if traditional image cross-correlation techniques are used to align the successive images, an entirely different morphology for a given feature can be produced (Figure 48b) for a highly textured material. A practical solution in such cases is to produce external feducial marks on the surface that can be used to align the images. For the reconstruction of fine features such as GB$\alpha$, it is not desirable to use Vickers indents for this purpose because of the fact that the errors introduced by large indents could be significant when compared to the dimensions of the
features of interest. Ideally, the dimensions of such external imprints should be significantly smaller in comparison to that of the features of interest.

The approach suggested by Randle et. al. [97] takes care of these issues because in this method, the sample is polished on two mutually perpendicular surfaces. Thus, the inclination of both traces can be determined with a high degree of accuracy. However, the subsequent steps in the process are tedious, and the experimental setup would become expensive and time-consuming. Moreover, this method can’t be used to produce site-specific information.

In the present work, two different three-dimensional methods have been developed to determine the local crystallographic orientation of a general GB plane that intersects the specimen surface by using two-surface trace approach. The accuracy of these methods has been evaluated on both cubic and hexagonal systems by using established crystallographic characteristics of special boundaries present in these systems.

4.3 Experimental Procedure

The validation of the proposed methods to determine the crystallographic orientation of an interface was performed using the known crystallographic characteristics of annealing twins present in a nickel based super-alloy, IN-100 and compression twins present in a deformed commercially pure (CP)-titanium sample. Deformation twins in a forged and annealed cylindrical bar of titanium (dimensions: 10.1 mm diameter 21.5 mm length) were produced by performing an interrupted compression test at room temperature with the strain rate of $1.4 \times 10^{-4}$ per sec.
Specimens for characterization were prepared using standard metallographic techniques with the final step involved vibratory polishing in a suspension of 0.05 μm Silica particles for a number of hours to achieve a mirror finish. For the optical microscopy, a standard Kroll’s etching agent (2 mL HF and 4 mL HNO₃ in 100 mL H₂O) was used to reveal the microstructure. The crystallographic orientations of parent phases and twins in IN-100 and CP-Ti systems were determined using EBSD data collection done in Philips XL30 ESEM FEG scanning electron microscope at 20kV, spot-size 4 and a working distance of 20 mm. Suitable step-size (~ 1 μm) in OIM TSL software was chosen to allow for the collection of data from a large area (~1 mm X 1 mm) in a reasonable amount of time. Also, the reliability of data collection was verified on a <100> Silicon sample under similar conditions. The two traces of an interface on mutually perpendicular surfaces were produced using FEI DualBeam™ focused ion beam (FIB)-Helios microscope, operated at 30 kV. Finally, the validation of the predicted orientations of twins was performed using TEM of site-specific thin-foils produced using Helios FIB microscope.

4.4 Results and Discussion

4.4.1 Proposal of Methods: Experimental Approach

An optical image is a two-dimensional section made through a three-dimensional microstructure. It thus cuts various microstructural features at an oblique angle and does not contain any information about their actual size distribution or morphology. In this
work, the actual orientation of grain-boundaries was determined by producing a site-specific section into the material to expose its trace on two mutually perpendicular surfaces. A combination of secondary electron imaging and focused-ion beam (FIB) in FEI NOVA Dual Beam™ (FIB/SEM) microscope was used for this purpose. Trenched sections were produced nearly perpendicular to the interface traces present on the sample surface using FIB. As shown by the schematic in Figure 49a the specimen surface was tilted to align perpendicular to the ion-beam prior to trenching. The trenched section was then imaged using a secondary electron beam detector, which was oriented at 52°. It was found that in general the inclination of a grain-boundary plane was not perpendicular to the surface (Figure 49b). A correction in the measured inclination of the trace of the interface on the trenched section (φ) was required because while the horizontal axis (AB) remains invariant during the rotation, the vertical axis undergoes a contraction (Figure 50). The actual depth AD and the projected depth of the trenched section AC are related by,

\[ AC = AB / \cos 38° \]  

(1)

Thus, with reference to figure 1b and figure 2b, the actual inclination ‘φ’ can be measured by,

\[ \tan \phi = \frac{\tan \phi'}{\cos 38°} \]  

(2)

The crystallographic orientation of the interfaces relative to the adjacent grain has been determined by combining their geometry with the crystallographic information provided by the EBSD data. Two separate methods based on two-surface trace analysis
have been developed for this purpose. The first method uses the explicit mathematical
description of the relationship between the sample reference frame and the
crystallographic reference frame of individual grains as defined in OIM-TSL software. In
the second method, the crystallographic values of the x-, y- and z- axes of EBSD frame
have been determined directly from OIM-TSL software, which have been subsequently
coupled with the geometrical characteristics of the traces of the interfaces.

**Method (a)**

In this method, the orientation of GB plane normal is initially determined in the
FIB reference frame. As shown schematically in Figure 51a, for two vectors \( \hat{v}_1 \) and \( \hat{v}_2 \)
that align along the trace of the interface on two mutually perpendicular surfaces, the
orientation of the normal to the interfacial plane is expressed by,

\[
\hat{n}_{\text{FIB}} = \frac{\hat{v}_1 \times \hat{v}_2}{|\hat{v}_1 \times \hat{v}_2|}
\]  

Subsequently, it is transformed relative to the EBSD reference frame. FIB and
EBSD reference frames are related by a rotation angle ‘\( \alpha \)’ about the common z- axis
(Figure 51b). Mathematically,

\[
\hat{n}_{\text{EBSD}} = \mathcal{R} \hat{n}_{\text{FIB}}
\]  

‘\( \mathcal{R} \)’ is the rotation matrix and is expressed by,

\[
\mathcal{R} = \begin{bmatrix}
\cos \alpha & -\sin \alpha & 0 \\
\sin \alpha & \cos \alpha & 0 \\
0 & 0 & 1
\end{bmatrix}
\]
In OIM-TSL software, the geometrical relationship between the sample reference frame and crystallographic reference frame of the given material is expressed in terms of Euler angles. The exact details of the geometrical relationship between the sample reference frame and the corresponding electron-image, as well as the definitions of the crystallographic reference frames for hexagonal and cubic crystals (Figure 52) are described elsewhere [85, 98]. In summary, these reference frames are related by,

$$\vec{r}_{EBSD} = g \cdot \vec{r}_{crystal}$$  \hspace{1cm} (7)

where $g$ is the orientation matrix that can be evaluated from Euler angles [84].

Thus, the orientation of an interface in the crystallographic reference frame of parent phase is calculated by,

$$\hat{n}_{crystal} = \vec{r}_{EBSD} \cdot \vec{r}_{crystal}$$  \hspace{1cm} (8)

**Method (b)**

The crystallographic values of x- and y-axes of EBSD frame are determined directly from the inverse pole figure (IPF) map. The vector-product of these directions produces the indices of z-axis or the plane-normal of the specimen surface. The crystallographic indices of reference directions are then combined with the known geometry of the interfaces to calculate their orientations in the parent phase. Stereographic projection provides an excellent platform to perform such analyses with considerable ease.

As shown in Figure 53a, the inclination ($\theta$) of the trace of interface is measured on the specimen surface relative to the x-axis of the sample reference frame. Its
inclination ($\varphi$) relative to the $z$-axis is measured in the trenched section. Here, angle $\phi$ in method-1 and $\varphi$ are related by $\varphi = 90^\circ - \phi$. Now since the trenched section has been produced approximately perpendicular to the interface, the angle that the grain boundary normal would make with respect to the surface normal [A] (or $z$-axis) would also be $\varphi$. In the stereographic projection (Figure 53b), a corresponding small circle at an angle ‘$\varphi$’ is produced about [A]. The location of the trace lying on the specimen surface is drawn on the stereographic projection relative to reference $x$-direction at an angle ‘$\theta$’. Finally, a line is drawn perpendicular to this trace and its intersection with small circle gives the orientation of interface plane-normal. A summary of steps involved is described below.

1. Measure the angle $\theta$ of the line of intersection for the grain boundary on surface 1 (trace-1)
2. Measure the corrected angle $\varphi$ for the line of intersection for the grain boundary on trenched surface 2
4. Determine the co-ordinates of $x$- and $y$- directions of the sample reference frame from the IPF map
5. Determine the crystallographic grain Normal [A] of the surface
6. Draw the stereographic projection with the grain normal [A] at the center and the $x$-axis pointing downwards
7. Draw the small circle at an angle $\varphi$ from the center corresponding to interface trace-2
8. Place the line of interface trace-1 at an angle $\theta$ relative to $x$-axis on the stereogram
9. Draw a normal to interface trace-1 passing through the center [A]

10. The intersection of this normal with the small circle drawn corresponding to the interface trace-2 is the grain boundary plane normal [A_N]

4.4.2 Validation of Methods

To determine if the proposed methods are accurate, the analysis was performed on special boundaries that possess known crystallographic characteristics, for both cubic and hexagonal systems. Figure 54 shows a low magnification back-scattered electron image of IN-100 alloy. The microstructure of this material consists of several annealing twins present in equiaxed grains. Previous research works [99] have established that twinning plane is of the type {111} relative to the parent phase. The analysis of EBSD map (Figure 55a) also showed that these twins were misoriented with respect to the parent phase by 60º about <111>. FIB trenches were sectioned on the interface between the twin and parent phases in locations 1 and 2 as highlighted in Figure 55. A corresponding image taken at 52º using the ion-beam (Figure 56) clearly delineates the interface.

Crystallographic and geometrical data used in both methods has been summarized in Table 3. Using method-1, the predicted crystallographic direction of the twin-plane normal for the location-1 is (102 106 100), which is misoriented approximately 2º relative to (111). For location-2, the indices are (-102 -100 113), which is misoriented approximately ~2.5º relative to (T T T).
Figure 57 shows the stereographic projection for the predicted orientation of twin using method-2. The predicted indices of the twin-plane normal at location 1 and 2 are close to (111) and (T T 1) respectively. Again, similar to method-1, a deviation of around 1°-2° is noted in this method as well. It should also be noted that the indices of twin-planes predicted by both methods are comparable.

A similar approach was adopted for the CP-titanium sample, which is a hexagonal close-pack (hcp) system. The engineering stress-strain plotted in Figure 58 shows that the test was interrupted when the sample had accumulated a compressive strain close to 12%.. The EBSD map of the sample shows the presence of compression twins in certain grains (Figure 59a). Sample was mounted such that the surface normal was parallel to the loading-direction during compression. A high density of twins oriented close to the [0001] direction in the inverse pole figure (Figure 59b) indicates the accommodation of strain along the c-axis by twinning. The morphology of a typical twin is shown in Figure 60.

All of the relevant data related to the geometry of the interface with respect to the parent phase as well as crystallographic information gathered from EBSD data have been summarized in Table 4. Using method-1, the approximate values of indices of the twin planes for both locations are (T 02) and (T T 2) respectively. As shown in Figure 61, method-2 also predicted the same indices for both cases. The nature of these twins was evaluated further using TEM studies. A site-specific TEM foil was sectioned at location-1. Figure 62 shows the interface between the twin and the matrix. The corresponding diffraction pattern comprises the scattering caused by both phases. Evidently, the mirror
plane or the twinning plane is along $[1 \bar{1} 02]$ and imparts a rotation of $85^\circ$ about $[1 1 \bar{2} 0]$. These results confirm the reliability of both proposed methods cubic and hexagonal systems. EBSD results indicated that in fact all the deformation twins present in the material are of type $\{1 \bar{1} 02 \}$. (Figure 63).

While these methods bear similarities to the method developed by Randle et. al. (1989), the overall approach is unique in a number of aspects. The production of a site-specific section at the desired location using FIB as opposed to conventional metallographic sample preparation makes these methods more versatile and simple for a variety of materials. The production of trenches approximately perpendicular to the trace of an interface on the sample surface simplifies the analysis and makes it easier to visualize the orientation of the GB plane relative to the sample surface.

However, these methods also suffer from certain limitations. For example, only those interfaces that intersect with the sample surface can be analyzed. A wavy boundary is difficult to analyze in such techniques. Three-dimensional techniques based on parallel serial sectioning and reconstruction protect all the information and can be used to reproduce the complete interface including small details of the geometry of an interface. Such details are difficult to retain in the proposed methods. Also, the production of a trench destroys an area around the region of interest. The reliability of these methods critically depends on the accuracy of the data collection using EBSD as well measurement of the geometry of the feature of interest. These errors get directly translated in the predicted indices of a general GB plane.
The small degree (≤ 3°) of deviation from the expected indices for both annealing and compression twins observed in this study can be attributed to a number of factors. These twins do not produce a flat interface in general and there may exist a certain degree of deviation from their ideal orientations of \{111\} and \{1\overline{1}02\} for cubic and hexagonal systems respectively. Also, errors in EBSD data-collection and measurement of geometry can further increase deviations that are difficult to segregate. Nevertheless, production of a small error (~3°) confirms the reliability of these methods.

4.5 Summary

The advent of modern tools such as, dual-beam FIB/SEM and EBSD has significantly simplified the site-specific analysis and characterization of materials systems. By combining them with other electron microscopy based techniques such as TEM a relationship between the crystallography and morphology across length scales can be understood with sufficient statistical reliability and ease. In the present work, these advanced techniques have been utilized to quantify the local crystallographic orientation of a GB plane relative to the adjacent parent matrix. Two methods have been proposed,

- Method (a) utilizes the mathematical descriptions of the relationship among EBSD and crystallographic reference frames, as defined in OIM-TSL software.
- Method (b) uses the direct crystallographic co-ordinates of X-, Y- and Z-directions of the sample reference frame and combines it with the geometry of the interfacial plane.
A low degree of deviation (<3°) from \{111\} annealing twins present in IN-100, and \{1\bar{T}02\} deformation twins present in a compressed sample of CP-titanium validate the reliability of the proposed methods.
Figures

Figure 45: Micrograph shows a variation in the trace of the grain-boundary plane upon polishing, which then used to determine its tilt angle and orientation in the sample reference frame.

Figure 46: Micrographs shows the reconstructed three-dimensional orientation of various interfaces by the serial-sectioning approach.
Figure 47: Micrographs show the method proposed by Randle et. al. [97], in which a combination of optical microscopy and EBSD has been utilized. However, this method can’t be used to extract site-specific information.

Figure 48: (a) Micrograph shows the anisotropic imprint produced by the Vickers indent, which introduces errors in the measurement of material-removal during sectioning, (b) in textured materials, the reconstructed morphology could be entirely different from the actual shape.
Figure 49: (a) Schematic show the orientation of Ion-beam relative to electron-beam in the microscope, and (b) trenched section made perpendicular to the grain-boundary shows the correct geometry of the interface that otherwise cannot be determined only from the specimen surface.
Figure 50: Schematic shows the in the projected secondary electron image, direction AB remains invariant while direction AC in the trenched section appears shorter (AD).
Figure 51: Schematics show (a) the definition of vectors ‘\(v_1\)’ and ‘\(v_2\)’ in the FIB reference frame and (b) the relationship between the FIB reference frame and the EBSD reference frame by the rotation angle ‘\(\alpha\)’ about \(Z_{\text{FIB}}\|Z_{\text{EBSD}}\) for a given interface.
Figure 52: Schematics show (a) the definition of the sample reference frame for EBSD data collection in TSL software, and (b) & (c) show the reference orientations of hexagonal and cubic systems with respect to EBSD reference frame [85, 98].
Figure 53: Schematic shows the methodology to determine the orientation of interface plane-normal [AN] using (a) geometrical characteristics of the interface on both surface as shown and (b) plotting them using a stereographic projection.
Figure 54: Micrograph shows the presence of annealing twins in the microstructure in IN-100 alloy. Also, the locations of two FIB trenches are highlighted.

Figure 55: (a) Micrograph shows the inverse pole figure map of IN-100 alloy. Here, (b) the pole figure for <100> single crystal Si wafer confirms the accuracy of data collection.
Figure 56: Micrograph shows the interface between twinned region and matrix on both trenched and sample surfaces in location-2.
Figure 57: Stereographic projections corresponding to (a) location-1 and (b) location-2 using method-2 predict the orientation of twin plane normals close to [111] and [T T 1].
Figure 58: Plot shows the compressive engineering stress-strain curve for cp-Ti.
Figure 59: (a) EBSD map shows the presence of compression twins in only certain grains in cp-Ti sample and (b) inverse pole figure in twinned region shows the accommodation of strain along c-axis. Locations ‘1’ and ‘2’ in (a) indicate the twins that have been analyzed.
Figure 60: Micrograph shows the morphology of compression twin at location-2 in CP-Ti sample.
Figure 61: Stereographic projection shows the inclination of GB plane for twins ‘1’ and ‘2’ in CP-Ti.
Figure 62: Micrograph shows the bright-field image of the twinned region in the parent phase at [1120] zone axis and corresponding diffraction pattern from both regions, which confirm that interface plane-normal, is of the type $\{10\bar{1}2\}$. 
Figure 63: EBSD analysis of compressed sample of cp-titanium revealed that all the deformation twins present in the material are of type $85^\circ/\{1\bar{1}0\}$. In other words, the twinning plane in all cases was found to be of the type $\{1\bar{1}02\}$.
### Tables

**Table 3**: Information related to the geometry of both traces of interface as well as orientation of parent grain and crystallographic indices of the axes of sample reference frame for IN-100 alloy is enlisted.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Geometrical details</th>
<th>Crystallographic details</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inclination of interface trace in FIB trench</td>
<td>Angle of interface trace with x-axis on specimen surface</td>
</tr>
<tr>
<td>1</td>
<td>66.8°</td>
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</tr>
<tr>
<td>2</td>
<td>-65°</td>
<td>96.9°</td>
</tr>
</tbody>
</table>

**Table 4**: Table gives a summary of data related to the geometry of both traces of interface as well as orientation of parent grain and crystallographic indices of the axes of sample reference frame for compressed CP-titanium sample.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Geometrical details</th>
<th>Crystallographic details</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inclination of interface trace in FIB trench</td>
<td>Angle of interface trace with x-axis on specimen surface</td>
</tr>
<tr>
<td>1</td>
<td>-51.2°</td>
<td>176°</td>
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<tr>
<td>2</td>
<td>49.5°</td>
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Chapter 5
Role of Grain-Boundary Parameters and Variant Selection on Thickening Characteristics of Allotriomorphic Alpha in Ti-550 Alloy

5.1 Abstract

Grain-boundary alpha (GB\(\alpha\)) is an unavoidable aspect of microstructural evolution in titanium alloys. It has a significant influence on subsequent phase transformations and the evolution of texture. These in turn affect the resultant mechanical properties, such as tensile ductility, high cycle fatigue crack growth and fracture toughness. The nucleation and growth of this phase is influenced by various grain-boundary parameters, namely the misorientation angle/axis and grain-boundary (GB) plane. In the present work, the anisotropic thickening behavior of GB\(\alpha\) phase at different grain-boundaries in Ti-550 alloy has been evaluated relative to GB parameters. Results indicate that in general, an appreciable contribution on thickening comes of the adjacent prior-\(\beta\) grain that establishes a Burgers-OR. A higher thickness is also statistically preferred at high angle grain-boundaries. In addition to misorientation angle, a significant contribution comes from the interaction of crystallographic orientation of GB plane with the selected crystallographic variant of GB\(\alpha\). In particular, a high thickness is observed in cases where grain-boundary normal oriented close to the broad face of the contributing Burgers orientation relationship (OR). For the given range of misorientation angles, thin
GBα gets produced for the cases when GB plane oriented away from the habit plane of the selected variant of Burgers-OR.

5.2 Introduction

The morphology of allotriomorphic or grain-boundary (GB) α phase in β-processed titanium alloys is known to deteriorate various mechanical properties e.g. high-cycle fatigue, ductility and fracture-toughness [1, 3, 58]. In addition, the evolution of Widmanstätten α phase gets affects by this phase [61, 63]. However, the factors that govern the evolution of a variation in the morphology or thickening of this phase at different grain-boundary are not understood. There are two important aspects of the evolution of this phase: geometric and crystallographic. From the crystallographic perspective, this phase produces a Burgers-OR with at least one of the adjacent β-grains [24]. In a β-grain, any of the twelve variants of α phase can be produced with equal probability. However at the grain boundary, a particular few are preferred, which leads to the phenomenon of variant selection [30, 42, 44].

It has been established that variant selection has an enormous impact on both, intra- and inter-granular precipitation. For example, Bhattacharyya et. al. [61] have discussed the role of variant selection on the morphology of both GBα and adjacent colonies of Widmanstätten α for specific misorientation angles between adjacent grains. It was shown that variant selection contributes to the formation of intra-granular colonies growing in the adjacent grains that have a common crystallographic orientation common to that of adjacent GBα. Notably, distinct growth morphologies of these colonies was
observed relative to the grain-boundary. Even in relatively fast-cooled microstructures, the morphology of Widmanstätten $\alpha$ adjacent to GB$\alpha$ produced a colony microstructure in the grain that produced a Burgers-OR. Intra-granular $\alpha$ adjacent to GB$\alpha$ on the other $\beta$-grain produced a basketweave microstructure [100].

From the geometric perspective, the grain-boundary parameters, namely misorientation angle/axis and GB plane are known to influence the variant selection. Stanford et. al. [44] have highlighted the importance of misorientation angle/axis in terms of the closeness of $\langle 101 \rangle$ poles of adjacent $\beta$ grains. An early nucleation of GB$\alpha$ has been generally observed for misorientation angle $> 22^\circ$ [58]. A high under-cooling is generally needed to nucleate GB$\alpha$ at low angle grain-boundaries. On the other hand, the orientation of GB plane has been proposed to be the most important factor on the variant selection occurring at grain-boundaries [42]. Statistically, it shows a preference towards orienting perpendicular to $[1 \bar{1} 1]_{\beta} \parallel [2 \bar{1} 1 0]_{\alpha}$, direction of the selected variant of GB$\alpha$.

Even though considerable amount of efforts have been made to understand the phenomenon of crystallographic variant selection, there evidently exists is a lack of studies that quantify the influence of these aspects on the morphology or thickening of these allotriomorphic precipitates. Most of such studies focus on the average growth response of these precipitate. In one such effort, the thickening of GB$\alpha$ has been proposed to occur by kink-on-ledge mechanism where the rate limiting step is the rejecter/accepter-plate mechanism (RPM) [28, 101]. In other words, the diffusion of various substitutional species along $\alpha/\beta$ and $\beta/\beta$ interfaces) has been proposed as the rate-controlling step. On the other hand, the nucleation of new growth ledges has been found
to be the rate controlling step for the thickening of intra-granular α phase [102]. These observations indicate an important contribution of grain-boundary parameters and variant selection on the evolution of GBα.

A variation in the thickness of GBα at different grain-boundaries in α/β–titanium alloys is a commonly observed and relatively unexplored aspect of microstructural evolution. The fact that GBα exercises a long range influence on the overall microstructural evolution and resulting properties makes such an effort important. Given the nature of the problem at hand, it is important to analyze a relatively large numbers of grain-boundaries for statistical reliability. In this chapter, the role of grain-boundary parameters as well as variant selection on the thickening characteristics has been explored and a relationship between the transformation texture and the thickness of GBα has also been established.

5.3 Experimental Procedure

The characterization and analysis of GBα was performed on Ti-550 alloy. Its chemical composition is: Ti–4(wt %)Al–4Mo–2Sn–0.5Si. A forged sample (dimensions~ 5mm x 5 mm x 15 mm) was initially heated at 1030°C for 2 hours in an inert (Argon) atmosphere to dissolve all of α phase and form β phase. It was subsequently slow cooled in the furnace to room temperature.

For characterization, the specimen was prepared using standard metallographic techniques with the final step involved vibratory polishing in a suspension of 0.05 μm
silica particles for a number of hours to achieve a mirror finish. For the optical microscopy, a standard Kroll’s etching agent (2 mL HF and 4 mL HNO₃ in 100 mL H₂O) was used to reveal the microstructure. The crystallographic orientations of α and β phases in the colony microstructure and at grain-boundaries were determined using EBSD data collection done in Philips XL30 ESEM FEG scanning electron microscope at 20kV, with a spot-size of 4 and a working distance of 20 mm. A suitable step-size (1.7 μm) in OIM TSL software was chosen to allow for the collection of data from a large area (~1.5 mm X 1.5 mm) in a reasonable amount of time. The reliability of this data collection was verified on a <100> silicon sample under similar conditions.

In Ti-550 alloy, the width of β-ribs in prior-beta grains was below the resolution limit of EBSD for the chosen step-size for the EBSD data-collection, making direct measurement of their orientations unfeasible. Instead, orientations of the intra-granular α phase were used to back-calculate the orientation of the parent β-grain by assuming the existence of Burgers-OR and using the expressions suggested by Glavicic and Humbert [103-105]. These expressions have been implemented with the quaternion parameterization of orientation space using the approach developed by Pilchak et. al [106]. At least three distinct orientations of α phase are required to determine the unique orientation of β phase.

The confirmation of the reliability of the calculation of β-phase was performed by collected a EBSD data at higher magnification and a smaller step-size of ~0.5 μm.

Collected EBSD data was used to determine the misorientation angles between adjacent β-grains at different grain-boundaries as well as to quantify the crystallographic
variant selected by GB\(\alpha\). In order to evaluate the contribution of the GB planes, the approach described in chapter-4 has been used, which combines EBSD, SEM and Dualbeam\textsuperscript{TM} FIB techniques. Finally, transmission electron microscopy (TEM) studies were performed on the interface of GB\(\alpha\) and \(\beta\) to confirm the reliability of the results obtained using EBSD data. For this purpose, site-specific TEM thin foils were sectioned using FEI Helios DualBeam\textsuperscript{TM} FIB microscope and were analyzed using Phillips CM200T microscope operated at 200kV.

5.4 Results and Discussion

5.4.1 Microstructural Evolution

The optical micrograph (Figure 64) shows the microstructure of Ti-550 alloy. Slow cooling from the \(\beta\)-solutionizing temperature results in the formation of a colony microstructure. Figure 65 shows the corresponding inverse pole figure (IPF) map. It shows the presence of large colonies of \(\alpha\) laths possessing the same crystallographic orientation, separated by thin \(\beta\) ribs. One large prior-\(\beta\) grain generally consists of more than one such colony. Grains boundaries get decorated by the allotriomorphic \(\alpha\) precipitates. The size-step for the EBSD data-collection was large (~1.7 \(\mu\)m), which made a direct determination of the orientations of various thin-ribs of \(\beta\)-phase unfeasible. Figure 66 shows the reconstructed orientations of different parent \(\beta\)-grains by back-calculations performed using the orientations of various intra-granular \(\alpha\) colonies. The approach used by Glavicic et. al. [104-105] has been used for this purpose. At least four
such colonies lying within a grain have been used to avoid an ambiguity. As evident from this micrograph, there still present a number of places where the automated MATLAB based subroutine, based on nearest neighbor approach [106], did not predict a unique orientation. Therefore manual calculations have been performed at all grain-boundaries not only to determine the correct orientations of β-phase at such grains but also to check the validity of all predicted orientations.

The accuracy these calculations was subsequently validated experimentally by performing EBSD data-collection at small step-size (~0.5μm) and high magnifications at some grains. Figure 67 shows one of such examples where the pole-figures of <101> and <111> poles of β-phase of highlighted grain in figure (a) is plotted. The experimental data closely matches with the pole-figures of the calculated data and confirms the reliability of both reconstruction and the back-calculation.

In general, these allotriomorphic precipitates produced a Burgers-OR with only one of the adjacent β grains (shown by pole-figures in Figure 68). In specific cases, a near Burgers-OR was established with both grains, due to low angle grain-boundaries. A variation in thickness as well as morphology of these GBα precipitates at different grain boundaries is evident in Figure 64. This observation is confirmed by the measurement of actual thickness in the trenched sections made using FIB (Figure 69). This micrograph also clearly show that in general, the GB planes produce obtuse angles relative to the specimen surface, which actually is a two-dimensional projection of a three-dimensional microstructure. Figure 70 shows the distribution of the actual thickness of various GBα precipitates. Out of 40 grain-boundaries analyzed, the maximum thickness measured was
The smallest thickness was close to 0.7 μm and the average thickness of these precipitates was found to be 2.5±0.9 μm. The formation of GBα precipitates led to a complete destruction of GB plane. Under the assumption that the growth of allotriomorphic α precipitates occurs predominantly along the grain-boundaries, the geometry of these precipitates has been used to determine the orientation of GB plane.

The GB plane is known to have an important role on the variant selection occurring at the grain-boundaries. In order to explore its potential contribution on the overall evolution of GBα precipitates, its crystallographic orientation relative to the adjacent grain that produces a Burgers-OR was calculated using methods described in chapter-4. These directions have been plotted as spots in a standard [001] stereographic projection (Figure 71). In this plot, the thickness of GBα has been incorporated by keeping the radius of these spots proportional to the corresponding thicknesses. Smallest and largest spots correspond to GBα thicknesses of 0.7 μm and 5 μm in this plot. Clearly, this plot does not clarify the role of GB plane and/or variant selection as different grain-boundary may produce a different variant of GBα phase. Plotting all these variants together in a standard [001] stereographic projection and drawing a conclusion proves daunting.

Furuhara et. al. (1991) solved this problem by assuming the production of one variant and determined the inclination of a GB plane relative to the variant selected. A similar strategy has been adopted in this study. GB plane indices were first transformed relative to the reference frame of the respective Burger-OR. Matrix transformation was again performed to produce a common variant, and the new inclination of GB plane was
determined. The overall approach to determine an orientation of a GB plane relative to the respective Burgers-OR is described below.

**Representation of GB plane in the reference frame of Burgers-OR using EBSD**

As shown in Figure 68, the presence of Burgers-OR can be qualitatively evaluated using pole figures, where $<101>$, $<111>$ and $<121>$ poles of adjacent prior-$\beta$ grains are superimposed with [0001], $<1\overline{1}20>$, $<10\overline{1}0>$ poles of GB$\alpha$ respectively. The prior-$\beta$ grain (that produces an orientation relationship) exhibits nearly superimposed poles of relevant vectors with the corresponding poles of GB$\alpha$. The specific poles that represent the production of orientation relationship can be determined directly in the sample reference frame from the pole figure, which are subsequently transformed in the crystal reference frame by using the equation (8) in chapter-4 that relates these two reference frames.

With regard to the crystallography of Burgers-OR, the fact that the directions for the Burgers-OR (i.e.$[1\overline{1}1]||[\overline{21}10]$, $(110)\,(0002)$ and$[1\overline{1}2]||[0\overline{1}10]$) orient nearly perpendicular to one other. This makes it an obvious choice for defining a rectilinear coordinate reference frame along these directions. By considering the spatial configuration of the superimposed pole figures of GB$\alpha$ and adjacent $\beta$ phase that exhibit a Burgers OR, clearly two different scenarios are possible. These configurations are shown in Figure 72, which are mirror images of each other. In the present work, configuration (b) has been chosen as a reference. Therefore all GB$\alpha$ exhibiting scenario (a) have been accordingly converted to configuration (b) to bring them on the same
platform. These configurations can be converted to one other by reversing the direction of the reference axis lying along \((110)_\beta\) \(\perp (0001)_\alpha\) and accordingly determining the direction along \([1\overline{1}2]\)\([0\overline{1}0]\) by taking a cross product. Table 4 shows a summary of the thicknesses of all GB\(\alpha\) considered, the corresponding crystallographic orientations of GB planes and their orientations relative to the selected Burgers-OR. Figure 73 shows the stereographic projection produced after transforming all GB\(\alpha\) with respect to a common Burgers-OR with \((110)_\beta\) \(\perp (0001)_\alpha\) along z-axis and \([0\overline{1}10]_\alpha\) along x- and y-directions respectively.

**Representation of GB Plane in Burgers-OR Reference Frame using TEM**

The reliability of the approach used to represent a GB plane in the reference frame of the respective Burgers-OR has been validated using TEM. Furuhara et. al. (1991) used the method of orienting the sample to produce a minimum projected thickness of an allotriomorphic precipitate and use the resultant orientation to determine its indices in the reference frame of Burgers-OR [42]. However this approach cannot be used in this system because of the high thickness of GB\(\alpha\) (>700 nm). Thick GB\(\alpha\) makes the variation in the relative projected thickness largely insensitive to the sample-tilt in TEM (Figure 74-Figure 75) because of the dimensions of a TEM foil is very thin.

In the present work, the features present at the interface of GB\(\alpha\) and prior-\(\beta\) grain with a Burgers-OR have been used. This approach is based on the trace analysis of these interfacial features. The exact methodology is described below.
Identify two non-collinear features (lines) lying on the GBα and prior-β interface.

Use three different crystallographic zones to produce their projected image and record the camera length and the magnification.

Individually perform trace analysis of both lines to determine their actual orientation in the crystallographic space. In this approach, images are collected close to the zone-axis (with a known ‘g’ vector) from three different beam directions. Afterwards, the resulting geometry of the projected defect is plotted in a stereographic projection relative to the ‘g’ vector utilized to image them. Finally, a great circle that intersects through all three points is plotted. The pole of this great-circle is the true line direction (u) of the line-defect. An error of ±5° is expected in this approach. The details of this methodology have been described elsewhere [93].

Perform a cross-product of each of the vectors using the stereographic projection to determine the orientation of the interface-normal that contains both features.

This exercise has been performed on multiple grain-boundaries. For illustration, two examples have been given in this section. Figure 76 shows the conscious effort taken to produce a relatively thick TEM-foil by using FIB to increase the surface of the interface as well as the ease of analysis using Kikuchi patterns.

As shown in the bright-field TEM micrograph in Figure 77 and Figure 80a the interface is rarely planar. Therefore a representative area was selected for further analysis, and two non-collinear features were identified. For both GBα, the three-zones used are: (a) [1\(\overline{1}\)1]_β || [\(\overline{1}\) \(\overline{2}\)10]_α, (b) [1\(\overline{1}\)00]_α and (c) [1\(\overline{1}\)01]_α (Figure 78a). The resulting interfacial
structures at these zone axes have been shown in Figure 78 and Figure 80b-d respectively for both grain boundaries.

The calculated orientations of grain boundary planes for both GB₀θ are shown in Figure 79 and Figure 81 respectively and have been compared with the results of the EBSD-based approach. Evidently, the calculated orientations of GB planes using both methods do not exactly match, and both produce some degrees of error. This deviation between two approaches can be attributed to the fact that in TEM, local curved orientations of the interface are analyzed while in the EBSD-based method, an average orientation of a grain-boundary plane is used. Nevertheless, the predicted orientations are close (< 10°) and confirm the validity of the methodology presented in this work using EBSD as well as transformations applied to express the crystallographic orientations of GB planes in the reference frames of respective Burgers-OR.

5.4.2 Influence of Grain-Boundary Parameters and Variant Selection

The matrix transformations performed to force all GB₀ precipitates to assume a single variant allows for an evaluation of an influence of GB plane on the variant selection and thickening. As shown in Figure 73, clearly, a large number of GB-planes orient perpendicular to \([1 \bar{1} 1]_β \parallel [\overline{2} 1 1 0]_α\) direction of the contributing Burgers-OR (with a deviation of ~15°-20°). These results are similar to the observations made by Furuhara et. al. (1991). However, a number of grain-boundaries also exhibited a deviation from this behavior, which suggests a need for modifications in the existing rules of variant selection.
This plot also indicates that grain-boundaries that produce thicker GB\(\alpha\) prefer to orient close to the \(y\)-axis (\(\langle 1\overline{T}\overline{T}\rangle_{\rho} \parallel \langle 0\overline{T}1\overline{0}\rangle_{\nu}\)) or the macroscopic broad face (\(~\langle 1\overline{T}\overline{T}\rangle_{\rho}\)) of Burgers OR. In order to clarify this observation, another stereographic projection was plotted (Figure 82). Here, the orientation of the terrace plane (\(\langle 1\overline{T}\overline{T}\rangle_{\rho} \parallel \langle 0\overline{T}1\overline{0}\rangle_{\nu}\)) was kept along the \(z\)-axis. The other major directions, \((1\overline{1}0)_{\rho} \parallel (0\overline{0}02)_{\alpha}\) and \([1\overline{T}1]\rangle_{\rho} \parallel [\overline{2}1\overline{1}0]_{\nu}\) were kept along \(x\)-and \(y\)-axis respectively. A thicker GB\(\alpha\) is observed in majority of those cases for which the GB plane aligned close to the broad face (within a deviation of \(~20^\circ\text{-}25^\circ\)). This behavior highlights one of the most important results that the prior-\(\beta\) grain that produces a Burgers-OR has a significant contribution on the thickening of GB\(\alpha\). This result is in contrary to a number of observations that have reported that incoherent regions of allotriomorphic precipitates are likely to grow faster [4].

Previous studies have reported that high angle grain-boundaries are the preferential sites for the nucleation of GB\(\alpha\) [58]. For the thermal treatment adopted in the present work, an earlier nucleation event at relatively higher temperature would imply an availability of higher thermal energy for both thickening and lengthening of these precipitates. Figure 83 clearly shows that the average thickness of GB\(\alpha\) increases at high misorientation angles between adjacent \(\beta\) grains. High misorientation angle boundaries are known to possess higher grain-boundary energy and diffusivity of solute atoms, which could contribute to faster growth.

On the other hand, relatively large error-bars especially at low and medium ranges of misorientation angles in Figure 83 and a scatter in the overall trend of thickening
characteristics observed in Figure 82, indicate overlapping contributions of GB plane and misorientation angles. It is thus imperative to account for misorientation angle in order to segregate the contribution of GB plane. This has been facilitated by color-coding the spots of GB planes according to the range of misorientation angles. With reference to the plot shown in Figure 83, the misorientation angles \( (\omega) \) have been conveniently divided into five broad categories: 1) \( \omega \leq 15^\circ \), 2) \( 15^\circ \leq \omega \leq 22^\circ \), 3) \( 22^\circ \leq \omega \leq 28^\circ \), 4) \( 28^\circ \leq \omega \leq 35^\circ \) and 5) \( \omega \geq 35^\circ \). Previous studies [58-59] have shown that the transition from a low angle boundary to a high angle boundary in titanium alloys occurs in the range between 15\(^\circ\) and 35\(^\circ\). This lack of a clear transition is the rationale for further subdividing the regime of misorientation angles. The modified plot is shown in Figure 84a. It is interesting to note that the extent of scatter of the GB plane away from the broad-face (center of stereographic projection) increases as the misorientation angle decreases. Most of the high angle boundaries, which produce thicker precipitates, orient closer to the center of the stereographic projection. However, for a given range of misorientation angle, thicker GB\(\alpha\) is clearly preferred for GB planes oriented close to the broad face. This observation is especially evident for misorientation angles smaller than 35\(^\circ\). An example of this phenomenon is shown in Figure 84b where grain-boundary (i) produces thicker precipitate in comparison to boundaries (ii) and (iii). The locations of these boundaries are indicated in Figure 84a. This result emphasizes that a GB plane affects both crystallographic and morphological aspects of the evolution of grain boundary precipitation.
The thickening of GB\(\alpha\) appears to get influenced by two important factors: variant selection (or Burgers OR) and grain boundary parameters (misorientation angle and GB plane). In the grain-interior, the morphology of Widmanstätten \(\alpha\) is solely dictated by the Burgers OR in the absence of external factors (e.g. grain-boundary parameters). Moreover, it has been shown by Aaronson et. al. [107] that thickening of both GB\(\alpha\) and Widmanstätten \(\alpha\) occurs by kink-on-ledge mechanism. However, the rate controlling step for the thickening of Widmanstätten \(\alpha\) is the nucleation of new ledges. In contrast, the rejecter/acceptor plate mechanism controls the thickening for GB\(\alpha\). Also, as observed earlier in Figure 65, Widmanstätten \(\alpha\) present of the prior-\(\beta\) grain (that establishes a Burgers-OR) adjacent to GB\(\alpha\) generally adopts the same crystallographic variant. Such a behavior provides an excellent opportunity to isolate and understand the roles of variant selection and GB parameters on the morphology of allotriomorphic precipitates.

The morphology of lamellar shaped \(\alpha\) phase is such that \([1\bar{1}12]_\beta\parallel[2110]_\alpha\) and \([1\bar{1}2\bar{1}]_\beta\parallel[0\bar{1}01]_\alpha\) directions of the Burgers-OR produce structural ledges on the broad face. Here, a significant growth occurs along the invariant line\([3\bar{3}5]_\beta\) in relation to other two major directions to produce a lath shaped precipitate. In the case of Ti-550 alloy, the morphology of Widmanstätten \(\alpha\) is generally that of a rectangular slab (Figure 85a) with one apparent minor growth direction (indicated by the red arrow). The crystallographic orientation of this direction relative to the variant selected was determined for a number of Widmanstätten \(\alpha\) colonies, using the EBSD and FIB based
approach described in chapter-4. The resulting plot is shown in Figure 85b-c, which confirms that the thickening of Widmanstätten α laths exhibits the least amount of thickening along the macroscopic broad face. A relatively large spread (10°-20°) in the plot can be attributed to errors in measuring the macroscopic orientation of the trace of the plates of various precipitates. These observations have also been confirmed by TEM based studies. Figure 86 shows the crystallographic orientation of the morphology of a Widmanstätten α plate corresponding to its minimum projected thickness, which demonstrates that the direction of minimum thickness lies close to the broad face of the Burgers-OR, which according to Figure 15.

The introduction of a GB plane provides a highway for the diffusion of various substitutional species and modifies the growth rate for GBα. The highest growth rate is observed when both major growth directions align with the trace of GB plane. In this configuration, the ‘broad face’ lies parallel to the GB plane. This phenomenon of this anisotropic growth has been schematically expressed by an ellipse (Figure 87). In this analysis, a diameter of the ellipse for a given orientation of GB plane represents its thickness. As an example, if both major growth directions lie along the trace of the GB plane, a thicker precipitate would form (shown by (i) in the schematic) corresponding to the major axis of the ellipsoid. If there is a contribution from the comparatively insignificant growth rate that occurs along the broad face, the thickness would decrease and the representative diameter will lie closer to the minor axis of the ellipse.

It is known that GBα establishes a Burgers OR with one adjacent grain and an irrational orientation relationship relative to the other. This study also suggests that the
‘Burgers’ grain probably has an important role on the evolution of GBα. A lack of understanding of the relationship present on the β-grain, which does not produce a Burgers-OR, makes the determination of the nature of the interface difficult, which is one of the limitations of the present study. It also explains the presence of a certain degree of deviation in the trends observed in the present work even after accounting for the variant selection, misorientation angle and GB plane.

Fortunately, certain special cases such as low misorientation angles (category-1 & category-2) as well as certain others configurations described by Bhattacharyya et. al. [61] produces a near Burgers OR relative to both grains. Such grain-boundaries offer an opportunity for an analysis of both α/β interfaces and could be useful for the evaluation of the proposed mechanism. In general three different possibilities exist: (a) the GB plane is away from respective macroscopic planes on both interfaces, (b) the GB plane is close to macroscopic planes at both α/β interfaces and (c) the GB plane orients close to macroscopic broad face with respect to one of the grains and away from it relative to the other. If the proposed mechanism is valid, it is expected that case (a) would produce a thin precipitate and cases (b) and (c) would produce a thick GBα phase. In Figure 88, such special boundaries have been plotted relative to the respective (near) Burgers OR for both adjacent grains. The highest measured thickness in the corresponding category of misorientation angles has also been plotted for a comparison. In particular, low and medium angle grain boundaries (shown by yellow and red spots) show that the orientation of the GB plane with respect to the habit planes of β-grains governs the thickening of GBα.
There are certain issues that have been encountered in the present work and have contributed to the unexplained scatter in the general trend. The approach used to study GB\(\alpha\) can only be used for the \(\beta\)-grain that produces a Burgers-OR. The contribution of adjacent \(\beta\)-grain that produced an irrational relationship cannot be addressed. Another major issue encountered of this study has been the approach of using the morphology of GB\(\alpha\) to determine the orientation of the corresponding GB plane. In such a developed microstructure, a complete destruction of the original GB plane occurred as a result of the precipitation of GB\(\alpha\) phase. The assumption that \(\alpha\) phase wets the grain boundary and preferentially lengthens along the interface has been the basis this approach. However, a three-dimensional study in a \(\beta\)-titanium alloy has shown that the growth and branching of GB\(\alpha\) can occur away from GB plane [60]. In addition, the reorientation of the GB plane occurs during the phase transformation and the morphology of GB\(\alpha\) may not necessarily align with it. A degree of scatter in the data is also caused by the inability to precisely determine the inclination of the interfaces at curved and wavy boundaries. The most important issue encountered in this study has been the inability to determine the role of misorientation axis on the evolution of GB\(\alpha\). Previous studies have shown the importance of the closeness of certain poles on the evolution of GB\(\alpha\), which is difficult to isolate in a well-developed microstructure used in the present work. Therefore there exists a need to understand the early stages of the precipitation of these precipitates, which can be relatively easily performed on \(\beta\)-titanium alloys and have been discussed in chapter-6. Despite these limitations, the observed data trends highlight the importance of GB parameters and variant selection on the evolution of allotriomorphic \(\alpha\) phase.
5.5 Correlation between Thickness of GBα and Morphology of Widmanstätten α

A commonly observed phenomenon in this work is shown in Figure 89, where it is observed that for the given range of misorientation angles, a geometrical relationship exists between the orientation of the GB plane with respect to the morphology of Widmanstätten α plates and the corresponding thickness of GBα. According to the schematic shown in Figure 90, if the angle (α) between the trace of the GB plane and the Widmanstätten α platelets is high, a thin precipitate evolves and vice versa for thick precipitates.

Previously, Bhattacharyya et. al. [61] reported the contribution of variant selection on the morphological relationship between GBα and adjacent Widmanstätten alpha for certain special cases in which GBα produced a Burgers OR with both grains. He used TEM analysis to determine the orientation of the trace of GB plane that aligned along the common [101] pole. In the present work, knowledge of complete GB parameters facilitates an expansion of this understanding to even general grain-boundaries. For example, the observed phenomenon of the geometrical dependence of GBα thickness and the morphology of adjacent Widmanstätten α relative to GB plane (Figure 90) can be understood by using the mechanism presented in this work.

Figure 65 has shown that Widmanstätten α precipitates close to GBα (on the β-grain that produced a Burgers-OR) generally tends to adopt the same variant as that of GBα, which contributes to the production of transformation texture. This directly implies that for the variant selected by GBα, the morphology of this adjacent Widmanstätten α
represents the ideal morphology. The presence of the GB plane forces GB$\alpha$ to deviate from this minimum energy configuration. Now, it has been shown that the morphology of intra-granular $\alpha$ is of that of a platelet or thin slab, where the minimum thickness is produced along the broad-face of the selected variant of Burger-OR. By combining this observation with the mechanism proposed in the present work, this geometrical relationship between GB$\alpha$ and Widmanstätten $\alpha$, which has been frequently observed in this work emerges. For example, a low angle between the GB plane and laths of Widmanstätten $\alpha$ would imply a small misorientation between GB$\alpha$ and the broad-face of the selected variant (Figure 90) and would produce a thick precipitate (Figure 89b). Similarly, a high angle of deviation would lead to a decrease in the thickness of GB$\alpha$ (Figure 89a). This behavior is a result of transformation texture present in titanium alloys and also serves an experimental example of thickening phenomenon observed in this study.

From a mechanistic perspective, the habit plane (which corresponds to the minimum thickness of Widmanstätten $\alpha$ and is perpendicular to the invariant line) of the Burgers-OR also represents the surface with smallest elastic stain energy [35], making it the most stable. It is therefore expected that a smaller angle between the habit plane and the GB plane would be a stable configuration and facilitate the growth of GB$\alpha$. At high angles, GB plane cannot support its growth over a long distance. This analysis of the morphological relationship of Widmanstätten $\alpha$ colonies adjacent to GB$\alpha$ in these general cases can easily be extended to the special cases.
5.6 Summary

GB\(\alpha\) is an important microstructural feature in titanium alloys. This study has shown that in \(\alpha/\beta\)-titanium alloy systems, its thickening characteristics depend upon grain-boundary parameters and their interaction with the variant selection. Following important results can be drawn from this work,

- A combination of GB plane and misorientation angle appears to have an important role on variant selection.
- The average thickness of allotriomorphic precipitates increases at higher misorientation angles.
- The grain that established a Burgers-OR with GB\(\alpha\) has a significant influence on thickening characteristics.
- The orientation of GB plane relative to the variant selection controls the thickening characteristics. Thicker GB\(\alpha\) are produced in those cases in which a GB plane orients close to the macroscopic broad face of the Burgers OR.
- Thickness of GB\(\alpha\) can be geometrically correlated with the orientation of adjacent Widmanstätten \(\alpha\) plates in the ‘Burgers’ grain, which is a direct outcome the presence of transformation texture present in the material.
Figure 64: Optical micrograph shows the development of a colony microstructure in Ti-550 alloy. Non-uniform thickness and morphology of GB$_\alpha$ at grain boundaries is evident.
Figure 65: EBSD map of the Ti-550 shows the crystallographic orientation of various colonies of α phase in different grains and grain boundaries. The arrows illustrate (refer text) the crystallographic relationship between GBα and Widmanstätten α.
Figure 66: Micrograph shows an automated reconstruction of β grains using the orientations of Widmanstätten α. This method produced occasionally inaccurate results at some locations, which required a manual calculations to rectify.
Figure 67: Experimental EBSD data of β phase of grain-B confirmed the accuracy of calculations performed to back-calculate the orientations of prior-β grains.
Figure 68: Pole figures show examples of the production of a near Burgers-OR with (a) one grain, generally for high angle boundaries and (b) both grains for low angle boundaries.
Figure 69: Cross-sectional FIB trenches made at various grain-boundaries show a significant variation in the thickness of GB\(\alpha\).

Figure 70: Plot shows the thickness distribution of the thickness of GB\(\alpha\).
Figure 71: A standard [001] stereographic projection shows the orientation of the GB plane in the crystallographic reference frame of a neighboring β grain that establishes a Burgers-OR.
Figure 72: Plot-figures show two types of spatial configurations of Burgers-OR.
Evidently, the scenario shown in (a) is same as that shown in (c), while scenario (b) is the mirror-image of it.
Figure 73: Plot shows the orientation of the GB plane relative to common Burgers OR.
Figure 74: Schematic shows that the relative change in the projected precipitate width ($t_1$) for a large precipitate upon tilting the TEM-foil is appreciably smaller than that for a small precipitate (mathematically, $(\frac{\Delta}{t_1}) < (\frac{\Delta}{t_2})$) for the same foil thickness ‘h’ and sample tilt ‘θ’ in TEM.
Figure 75: Plot show an increase in the relative projected precipitate-width at higher tilt angles for 150 nm thick TEM foil. Thickness increments become nearly insensitive for precipitate-size $> 1 \, \mu m$. 
Figure 76: Micrographs show the thickness of GBα and the steps taken to produce a TEM foil using a dual beam FIB, and the location of the β-grain that produced a Burgers-OR.
Figure 77: Bright-field TEM micrograph shows a variation in location inclination of the GBα-β interface and also indicates the region where analysis has been performed.
Figure 78: (a) Schematic shows the relationship between different zones, where the trace analysis of two non-collinear lines indicated in micrographs corresponding to (b) $[1 \bar{T}1]_\beta \parallel [1 \bar{2}10]_\alpha$, (c) $[1 \bar{T}00]_\alpha$ and (d) $[1 \bar{T}01]_\alpha$ has been performed.
Figure 79: Stereographic projection shows that the calculated GB normal using TEM-method (highlighted by the blue circle) is reasonably close to the one predicted by the EBSD (indicated by the red spot) method.
Figure 80: Micrographs show (a) the location chosen for the trace analysis at (b) $[\overline{1}1\overline{1}]_\beta$ $|[\overline{1}2\overline{1}0]_{\alpha'}$, (c) $[\overline{1}1\overline{0}0]_{\alpha}$ and (d) $[\overline{1}1\overline{0}1]_{\alpha}$ zones respectively.
Figure 81: Stereographic projection show the comparison of the orientation of GB plane calculated using TEM-method (highlighted by the blue circle) and EBSD method (shown by the red spot).
Figure 82: Stereographic projection plotted about \([1\overline{1}2]\beta \parallel [0\overline{1}0]\alpha\) of the Burgers-OR shows the clustering of relatively thick precipitates close to the center.
Figure 83: Plot shows an increase in the average thickness of GBα precipitates as a function of the ranges of misorientation angles (θ) where, (1) $0^\circ \leq \theta \leq 15^\circ$, (2) $15^\circ \leq \theta \leq 22^\circ$, (3) $22^\circ \leq \theta \leq 28^\circ$, (4) $28^\circ \leq \theta \leq 35^\circ$ and (5) $\theta \geq 35^\circ$. 
Figure 84: (a) Incorporation of misorientation angle (\(\omega\)) in the stereographic projection plotted relative to broad face of Burgers OR confirms that within a given range of \(\omega\) values, the formation of a thick GB\(\alpha\) is preferred for GB plane oriented close to the broad face. (b) Micrographs indicate that for misorientation angles of category-3, thickest precipitate is formed at the location (i). Here the smallest thickness is \(\sim 0.7 \ \mu m\) and the highest thickness is \(\sim 5 \ \mu m\).
Figure 85: (a) Morphology of Widmanstätten \(\alpha\) in Ti-550 alloy can be described by an infinite lath. A growth direction indicated by red arrow corresponds to minimum growth, which orients towards the broad face of the Burgers-OR as indicated by the stereographic projections in the (b) sample reference frame as well as (c) in the reference frame of Burgers-OR.
Figure 86: Bright-field TEM micrograph corresponding to the smallest projected thickness of Widmanstätten $\alpha$ plates was found at around 14° away from $[1 \bar{1} 2]_\beta \parallel [0 \bar{1} 10]_\alpha$ of Burgers-OR.
Figure 87: Schematic shows the mechanism for the thickening of GB\(\alpha\) can be indicated by the diameter of an ellipse. The lath morphology is modified by the GB plane. Plane ‘\(ab\)’ produces the thickest precipitate of relative width ‘\(AB\)’ while ‘\(cd\)’ produces a thinnest precipitate of relative width ‘\(CD\)’.
Figure 88: Stereographic projection for cases that produce a near Burgers OR with both grains shows the formation of thick GBα when the GB plane orients close to the corresponding broad face relative to at least one of the grains.
Figure 89: Micrograph shows an example of a geometrical relationship between Widmanstätten $\alpha$ and the thickness of GB$\alpha$ for a misorientation angle $\sim 18^\circ$. A high angle between platelets of Widmanstätten $\alpha$ and the trace of GB plane on ‘Burgers’ side (indicated by arrows) corresponds to ‘thin’ GB$\alpha$ in (a) and vice versa in (b).

Figure 90: Schematic shows that thickening of GB$\alpha$ is geometrically related to Widmanstätten $\alpha$ present on the grain that produces an OR by an inclination angle $'\alpha'$. 
Table 5: A summary of GB orientations in crystal and Burgers-OR reference frames.

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Chapter 6
Influence of Grain-Boundary Parameters on Variant Selection and Morphology during Early Growth Stages of Allotriomorphic Alpha in Ti-5553 Alloy

6.1 Abstract

The morphology and variant selection occurring during the early growth stages of gbα in titanium alloys has the potential to influence the evolution of both the Widmanstätten α plates and transformation texture. In the present study, both of these aspects of the evolution of gbα have been evaluated with respect to grain-boundary parameters, namely the misorientation angle/axis and grain-boundary (GB) plane in Ti-5553 alloy. Results indicated that an early nucleation and growth of these precipitates is primarily controlled by misorientation angle/axis. The precipitates preferentially nucleated for which one of the <111> and/or <101> poles of adjacent grains oriented close to one other. As compared to the GB plane, these conditions also dominated the phenomenon of variant selection and severely short-listed the allowed variants of gbα. The nucleation of gbα generally occurred for misorientation angles ≥ 20°. Subsequently, the interaction of variant selection and GB plane played a dominant role on the morphology of these precipitates. Continuous precipitates were produced when the GB plane-normal oriented nearly perpendicular to [1 1 1]β || [ 1 1 1 ] of the Burgers orientation relationship (OR). Finally, a general similarity of the allotriomorphic transformations has
been established for $\alpha/\beta$-systems by comparing these results with those obtained for Ti-550 alloy.

6.2 Introduction

The development of the overall microstructure in titanium alloys during diffusion-controlled $\beta$-processing is initiated by the formation of and is significantly governed by the grain-boundary $\alpha$ (GB$\alpha$), which is the first phase to heterogeneously nucleate at grain-boundaries and triple-points. Therefore, it is important to understand and quantify the factors that control the early stages of the evolution of this phase. In this chapter, the contribution of grain-boundary parameters, misorientation angle/axis as well as grain-boundary (GB) plane, has been evaluated with respect to the propensity for the preferential nucleation and growth. In addition, their contribution on the crystallographic variant selection has been evaluated. It has already been proposed in chapter-5 that in $\alpha/\beta$-titanium alloys, the interaction between the GB plane and variant selection likely governs the thickening characteristics of these precipitates. However, the possibility of early nucleation of GB$\alpha$ at certain grain-boundaries is expected to provide an additional thermal energy, which could provide an alternate explanation for the enhanced growth of certain allotriomorphic precipitates. Other studies have demonstrated that both misorientation angle/axis [58] and GB plane [91] can contribute to the early precipitation of this second phase at grain-boundaries. Therefore it is important to isolate the particular
effect of particularly misorientation angle/axis on this phenomenon so that the
correlation of GB plane on thickening and morphology can be established.

It is well known that $\alpha$ phase produces Burgers-orientation relationship (OR) with
the parent $\beta$ phase, which is characterized by the parallelism of one of \{101\}_$\beta$ with \{0001\}_$\alpha$
and close pack directions: \langle 1\bar{1}1 \rangle and \langle 2\bar{1}10 \rangle. This in turn allows for the
production any one of twelve variants in the grain-interior that are equally probable.
However, GB$\alpha$ exhibits a preference for certain few variant(s), which leads to the
phenomenon of crystallographic variant selection. Various studies have been carried to
understand the role of GB parameters on this phenomenon. Furuhara et. al. [42]
attempted to quantify the contribution of GB plane. Stanford et. al. [44] etc. have
proposed the importance of misorientation angle/axis. Evidently, there exists a need to
quantify the role of all GB parameters to develop a comprehensive understanding about
the relative dominance of these two aspects of the GB character.

Thus, the scope of this work is to evaluate the contribution all GB parameters on
early nucleation and growth, variant selection and the development of morphology of
GB$\alpha$ in Ti-5553 alloy. A $\beta$-titanium alloy was chosen for for this analysis because is the
in these alloys, the $\beta$ phase can be retained upon applying a thermal quench. This
significantly simplifies the analysis both experimentally and computationally. Such a
study is difficult in a near $\alpha$- or $\alpha/\beta$- alloy systems because of the propensity to produce
Martensite. Finally, a comparison with the evolution of GB$\alpha$ in a Ti-550 alloy has also
been made to: (a) show the validity of observations made on $\beta$- titanium alloy for
similarly processed $\alpha/\beta$– titanium alloys, (b) isolate the contribution of misorientation angle/axis on the thickening characteristics of GB$\alpha$, which would in turn help to isolate the contribution of the GB plane for both Ti-5553 and Ti-550.

6.3 Experimental Methods

The chemical composition of Ti-5553 alloy used in this study is: Ti-5(wt%)Al-5Mo-5V-3Cr-0.5Fe. As-received forged material was sectioned to produce four samples (dimensions~20mm x 20mm x 40 mm) for the thermal treatments. All samples were initially $\beta$-annealed at 1000°C for 15 minutes in an inert (Argon) atmosphere ($\beta$ to $\alpha$ transition temperature~850°C). Afterwards, each sample was separately cooled in the furnace at the controlled rate of 5°C/minute to (a) 825°C, (b) 800°C, (c) 775°C and (d) 750°C respectively. All four samples at these four different temperatures were soaked for 2 hrs to allow for the phase transformations to occur and finally they were water-quenched to room temperature.

Another heat-treatment that has been considered in this work consisted of $\beta$-annealing the sample at 1000°C for 15 minutes and water-quenched. Material was then heated back to 650°C at 5°C/min and soaked for 2 hrs. Finally it was water-quenched to room temperature.

All samples were prepared using standard metallographic techniques for the characterization, in which the final step involved polishing in a suspension of 0.05 μm Silica particles for a number of hours to achieve a mirror finish. Samples were characterized using an FEI Sirion scanning electron microscope (SEM) at an operating
voltage of 10kV, spot-size 4 and a working distance of 4 mm. The crystallographic orientation of both \(\alpha\) and \(\beta\) phases was gathered at various locations using electron back-scattered diffraction (EBSD) technique in an FEI-environmental SEM at 25 kV, a spot-size 4, working distance of 20 mm and step-size of 0.5 \(\mu\)m. The accuracy of the data-collection was validated using a \(<100>\) single crystal wafer of silicon. Finally the local orientations of the GB planes were determined by producing sections using focused ion beam (FIB) nearly perpendicular to the trace of grain-boundaries (in this case, GB\(\alpha\)) present on the polished surface of the specimen. Subsequently, the orientations of the GB plane in the crystal reference frames were determined using the approach described in chapter 4.

6.4 Results and Discussion

6.4.1 Microstructural Evolution

The low magnification images in Figure 91 shows the progression of the evolution of microstructure with an increase in under-cooling (temperature below the \(\beta\) to \(\alpha\) transition temperature of 850°C): (a) 825°C, (b) 800°C, (c) 775°C and (d) 750°C. Evidently, a higher under-cooling produced a greater amount of \(\alpha\) phase. In addition, greater under-cooling resulted in a larger fraction of the grain-boundaries being covered with \(\alpha\) and a greater propensity to produce the Widmanstätten \(\alpha\) plates. As shown in the higher magnification micrograph in Figure 92, at 825°C (25°C below the \(\beta\)-transus) the formation of \(\alpha\) phase was registered only at isolated places. As expected for such early stages of the evolution of the microstructure, the precipitation was observed only at grain-
boundaries and of intra-granular $\alpha$ phase did not form (Figure 91a). At 800°C, some increase in the amount of $\alpha$ phase was observed. Again, no intra-granular precipitation was seen. Interestingly, certain grain-boundaries appeared to show a preference for the early nucleation and growth (Figure 93a). At these grain-boundaries, the morphologies of these allotriomorphic precipitates were found to be of two major types: (a) continuous, (b) discrete. Here, the continuous precipitates have been defined as the ones with large aspect ratios while discrete particles have small aspect ratios (Figure 93b). In general, the precipitation of GB$\alpha$ contributed to some degree of deviation of the grain-boundaries from their original configurations. Also, along the same boundaries, the deviation of GB plane appeared to convert a relatively continuous morphology to a discrete one.

As shown in Figure 91c, at 775°C, a large increase in the amount of the overall coverage of the total grain-boundaries was observed. It should be noted that an addition under-cooling of 25°, there is a large increase in amount of $\alpha$ phase in the material. In addition, the precipitation of Widmanstätten $\alpha$ plates became evident at this temperature. It is interesting that the formation of this intra-granular $\alpha$ precedes the formation of GB$\alpha$ at certain grain-boundaries (Figure 94). Finally at 750°C, GB$\alpha$ decorated nearly all of the grain-boundaries. In addition, a significantly higher amount of Widmanstätten $\alpha$ adjacent to GB$\alpha$ was produced (Figure 95). These observations suggest that $\alpha$ phase precipitates first at the grain-boundaries; at higher under-cooling the precipitation of intra-granular $\alpha$ occurs preferentially close to GB$\alpha$ and produces Widmanstätten morphology. There have been only isolated instances in which $\alpha$ phase was produced in the grain-interior for such slow cooling rates.
Thus, amongst various heat-treatments performed in this work, the early stages of the evolution of GBα have been captured in the heat-treatment (b) for which, after β-annealing at 1000°C, the sample was kept at 800°C for 2 hrs and water-quenched. This heat-treatment has been chosen for analyzing the evolution of allotriomorphic α relative to grain-boundary parameters.

The fifth heat-treatment that involved water-quenching the sample from the β-annealing temperature (1000°C) and heating it back at a slow rate (5°C/min), produced an entirely different microstructure. In this heat-treatment fine precipitates of elongated α phase gets produced in the grain-interior (Figure 96). The precipitation of allotriomorphic α at low temperatures does not allow the grain-boundary to reorient. Morphologically, ‘continuous’ and ‘discrete’ GBα precipitates have been observed in this heat-treatment.

6.4.2 Early Precipitation Characteristics: Variant Selection and Morphology

**Contribution of misorientation angle/axis**

For the heat-treatment (b), Figure 97 shows some examples of the EBSD data collected around those particular grain-boundaries at which GBα precipitated. On correlating the precipitation sites with the corresponding misorientation angle/axis, it has been found that GBα tends to form at high angle grain-boundaries where misorientation angle (ω) exceeds ~20°. Figure 98 shows the fraction of GBα precipitated at different ranges of misorientation angles. The fraction precipitated at low angle grain-boundaries was very small. A maximum in the amount of GBα is achieved for 40°≤ω<50°. The
presence of a negligible fraction of GBα at low angle grain-boundaries can be explained by the fact that a low GB energy provides a smaller driving force for the precipitation. The greatest amount of GBα for $40^\circ \leq \phi < 50^\circ$ is established, which matches well with the highest misorientation angles for a random microstructure (Figure 99).

It is well known that GBα produces a near Burgers-OR with at least one of the neighboring β grain. In order to identify the grain that produced this OR, pole figures of $<110>$, $<111>$ and $<112>$ of both β grains and [001], $<\bar{2}110>$ and $<10\bar{1}0>$ of the corresponding GBα are superimposed and analyzed. For certain values of misorientation angle/axis, GBα establishes a near Burgers-OR with respect to both of the adjacent grains. These cases are: $10.5^\circ/\langle110\rangle$, $60^\circ/\langle111\rangle$, $49.48^\circ/\langle110\rangle$ and $60^\circ/\langle110\rangle$ [61]. An example of this phenomenon is shown in Figure 100, where the misorientation angle between blue and yellow grains is $60^\circ/\langle110\rangle$ and it produced a continuous layer of GBα. For other more general cases, GBα generally establishes a near Burgers-OR with one of the adjacent grains. In general, two distinct characteristics were found to dominate the preferred sites for the early precipitation of GBα. These are: (a) close $<101>$ poles and (b) close $<111>$ poles of adjacent β-grains. Examples for each of these cases have been shown in Figure 101. Close $<101>$ and $<111>$ poles for all the GBα precipitates were super-imposed, and were color-coded according to the range of misorientation angles. Interestingly, it was found that most of the close $<111>$ that contributed to the formation of GBα preferred to cluster in the misorientation angles of $25^\circ \leq \phi < 40^\circ$. In contrast, near $<101>$ poles were dominant in $40^\circ \leq \phi < 55^\circ$ (Figure 102).
These observations clearly indicate the importance of two aspects of the misorientation angle/axis. These are (a) minimum misorientation angle (b) closeness of $<101>$ and $<111>$ poles of adjacent grains. Both of these aspects are required to explain the early precipitation behavior. Misorientation angle decides the GB energy and therefore reduces the material’s propensity to nucleate a second phase at low angle grain-boundaries. The closeness of the relevant poles of adjacent grains appears to be the dominant criterion for the nucleation of $\text{GB}_\alpha$. At low angle grain-boundaries, all the poles of adjacent grains orient close to one other (Figure 103). However, the combined influence of low misorientation angles and a small fraction of such boundaries in a random microstructure (Figure 99) results in less precipitation.

On the other hand, there exists an anisotropic precipitation response at high angle grain-boundaries. Thus, it is important to understand the distribution of the minimum angles between these poles of the adjacent grains at different misorientation angles. Figure 104 shows the normalized frequency for both $<111>$ and $<110>$ for a random microstructure that are related by angles smaller than $10^\circ$. Evidently, close $<111>$ poles show a slightly higher distribution for $25^\circ \leq \omega < 40^\circ$ and close $<110>$ poles become dominant for $40^\circ \leq \omega < 48^\circ$. With reference to the actual population of each of these close poles, the fact that there are higher numbers of $<101>$ poles (twelve) as compared to $<111>$ poles (eight) in a body-centered cubic crystal explains why there are more instances for the presence of low angles between $<110>$ poles (Figure 104b). However, these observations are not sufficient to explain the dominance of precipitation events at close $<111>$ in the misorientation angles between $25^\circ$ and $40^\circ$ and between $40^\circ$
and 54° for the close <110>. More studies need to be carried out to understand the role closeness of these poles plays on the precipitation of GBα.

Interestingly, it has also been observed that, under suitable grain-boundary conditions, multiple crystallographic variants of GBα can be produced on a single grain-boundary, even in such slow-cooled microstructures. As shown in Figure 105, the grain-boundaries between pink (grain-C) and two purple grains (grain-A and B) produced a coincidence site lattice (CSL) index of 13b (~27.8°/<111>). Despite producing a low-energy interface, again the close <111> poles of adjacent grains produced various GBα precipitates on the same boundary. In this case as well, the common <111> as the misorientation axis also contributed to the variant-selection for all GBα precipitates. These variants were produced relative to both grains in an alternate fashion. In this case, the common <111> (also the misorientation axis) produces three <101> directions that orient perpendicular to it and produce 60° with respect to one other. For this particular case, a misorientation of nearly 30° about the same <111> relative to an adjacent grain makes six <101> poles misoriented by nearly 30° and having an orientation along the trace of the <111> pole, as shown in Figure 106. Out of possible six variants, five have been observed. These observations challenge the current understandings about the existing rules of variant selection that propose the existence of a unique variant at a given grain-boundary.

For the special case in which grain-boundaries are misoriented by 60° about <110> (Figure 100), GBα produces a near Burgers-OR with both grains and adopts a low energy configuration. Even for general cases, the close <111> and <101> poles of
adjacent grains contributed to the variant selection, as shown in Figure 101. It was found that out of 35 grain-boundaries that have been analyzed in the present work, nearly 85% GBα showed the dominance of misorientation angle and axis on the variant selection. Even for the cases in which a deviation was observed, the closeness of <111> and/or <101> poles was registered. However, in such cases these close poles did not contribute to the variant selection. Figure 107 shows one example each for the close <111> and close <101> cases.

These observations clearly indicate the dominance of misorientation angle/axis on the variant selection. This phenomenon can be explained by the fact that during the early growth stages of a slow cooled microstructure, a small GBα precipitate would produce a small interfacial area with the adjacent β-grains, which would make the contribution of GB plane relatively less important with respect to both early nucleation and variant selection. A direct implication of this phenomenon is that it severely short-lists the number of allowed variants GBα can adopt. There are six allowed variants for close <111> poles as each such pole is perpendicular to three <101> directions (Figure 108). In contrast, close <101> poles would present only four possible variants for further short-listing.

Subsequently other conditions (GB plane etc) set in to further reduce the allowed variant at a given grain-boundary. In order to determine the contribution of a GB plane, the methodology of producing a site-specific FIB-section perpendicular to the grain-boundary, as described in chapter 4 has been used.
Contribution of Grain-Boundary Plane

FIB trenches were used to expose three-dimensional morphologies of GBα precipitates at different grain-boundaries, as shown in Figure 109. These morphologies have been divided into (a) continuous and (b) discrete categories. In order to evaluate the contribution of GB plane, its normal was calculated using the methods described in chapter 4. It has been shown in Figure 93 that a certain degree of reorientation of grain-boundaries occurs as a result of the allotriomorphic precipitation. In order to take into account this change, FIB sections have been produced nearly normal to the site-specific projection of trace of GBα, an example of which is shown in Figure 110. Subsequently, similar to the approach described in chapter 5, the orientations of the GB planes were determined relative to their respective Burgers orientation relationships and were again transformed with respect to a common variant. The resultant stereographic projection has been shown in Figure 111.

As evident from this figure, the GB plane shows a preference (~50% cases) for orienting nearly perpendicular to [1\overline{1}1]_\beta, [2\overline{1}0]_\alpha of the common Burgers-OR. This observation is similar to the results published by Furuhara et. al. (1991). These observations have been used to propose the importance of GB plane on variant selection. However, in this plot there still exists a significant population of GBα that orient away from this orientation. Therefore the dominance of GB plane on the early precipitation and the variant selection was not established under these processing conditions. On the other hand, the presence of a continuous GBα layer at a low angle grain-boundary (shown by the grey spot) indicates that the GB plane might exercise some degree of influence. It is
already reported that the GBα phase does not prefer to nucleate at low angle grain-boundaries. However in this case the presence of GBα corresponds to an important characteristic, namely that the GB plane orients very close to the habit plane of Burgers-OR. Various previous studies have reported the importance of the alignment of GB plane with the habit-plane as a criterion for an early nucleation of a second phase [91]. Thus, it is possible that the GB plane plays a role in the early nucleation of allotriomorphic precipitates is possible, even for the slow-cooled microstructures. At the high angle grain-boundaries, the contribution of the GB plane has been analyzed in those cases for which the presence of close <111> and/or <101> did not contribute to the variant selection of GBα. These cases constitute only ~10%-15% of all the cases analyzed. As shown in Figure 112, GB plane orients nearly normal to \([1\bar{1}1]_\beta \parallel [2\bar{1}10]_\alpha\) of the contributing Burgers-OR in all these cases. These observations indicate that the relative dominance of misorientation angle/axis and GB depends upon thermo-mechanical processing conditions. Under suitable conditions it is possible to produce a dominant contribution of GB planes.

With regard to the morphology of GBα, Figure 111 also shows that a discrete morphology is generally produced when the GB plane orients close to \([1\bar{1}1]_\beta \parallel [2\bar{1}10]_\alpha\). A continuous morphology is produced in all those cases for which the GB planes oriented away from this direction. The color-coding of GB-planes according to the misorientation angle/axis in the same plot confirms that the morphology of GBα is controlled by the inclination of GB plane relative to variant selection. Misorientation angle/axis does not
appear to directly influence this aspect of the evolution of GB\textsubscript{\(\alpha\)} as there is no preference for a particular range of misorientation angle in this regard.

However, misorientation angle/axis could still play a role on this morphology through variant selection. As observed earlier, misorientation angle/axis dominates the variant selection in a majority of cases. It is therefore possible that the short-listed variants force the GB plane to orient towards \([1\bar{T}1]_\beta \parallel [2\bar{T}0]_\alpha\). A comparative example for this phenomenon is shown in Figure 113. With respect to both of the adjacent \(\beta\) grains, there exist twenty-four possible variants that GB\textsubscript{\(\alpha\)} can choose from. However, upon applying the condition of the dominance of misorientation angle/axis, there are only six allowed variants (highlighted by the red circles). In the first case, this condition produced all of these variants towards \([1\bar{T}1]_\beta \parallel [2\bar{T}0]_\alpha\). GB\textsubscript{\(\alpha\)} had to choose one of these allowed possibilities and produced a ‘discrete’ morphology. In the second case, GB plane has an option to choose orientation, and is nearly perpendicular to \([1\bar{T}1]_\beta \parallel [2\bar{T}0]_\alpha\). Thus, it produces a ‘continuous’ morphology. Clearly, misorientation angle/axis has an indirect influence on the morphology of GB\textsubscript{\(\alpha\)} through the phenomenon of variant selection.

It is known that the existence of a Burgers-OR imposes a lath-shaped morphology on the \(\alpha\) phase, with a major growth occurring along the crystallographic invariant line (which is normal to the habit plane). Therefore, corresponding to each of the twelve variants, there are twelve distinct growth directions of \(\alpha\) in the grain-interior. At the grain-boundaries, a combination of misorientation angle/axis and GB plane determines
the variant selection, which decides one of these twenty-four (relative to both adjacent grains) morphologies of chosen variant in the grain-interior. This morphology is exhibited by the adjacent Widmanstätten $\alpha$ on the $\beta$-grain that establishes a Burgers-OR, which generally chooses the variant selected by GB$\alpha$ (Figure 114). The presence of the GB plane then interacts with this morphology and makes the GB$\alpha$ phase deviate from this growth direction. In this process, the GB plane also undergoes a re-orientation. As shown by the schematic in Figure 114A, if GB plane orients close to the habit plane of the Burger-OR, it does not reorient much and supports the growth of GB$\alpha$ over large distances. Instead, if variant selected orients the GB plane away from the habit plane, the growth of GB$\alpha$ occurs away from its ideal growth direction and significantly reorients the GB plane (Figure 114B). At the curvature beyond which the GB plane cannot reorient any further, the growth of GB$\alpha$ becomes unstable because this orientation has not been the ideal growth direction. Thus the growth of GB$\alpha$ stops and produces a ‘discrete’ morphology. Any further transformation can only occur by nucleation at other places along the grain-boundaries and/or by the precipitation of adjacent colony $\alpha$ plates.

6.4.3 Morphology of GB$\alpha$ in Water-Quenched and Aged Sample

Figure 96 shows that morphologically, GB$\alpha$ can produce a ‘discrete’ or ‘continuous’ precipitates at different grain-boundaries. By producing FIB sections at different grain-boundaries, it is possible to observe the three-dimensional morphologies of these precipitates (Figure 115). The inability of grain-boundaries to reorient severe
restricts the continuity of GB\(\alpha\) layers. The presence of smaller crystallographic pockets of GB\(\alpha\) phase can be observed from the channeling contrast in the back-scattered SEM images shown in Figure 96. Morphologically or geometrically, these pockets are connected and therefore have been termed continuous precipitates. It is well known that \(\alpha\) and \(\beta\) phases are related by the Burgers-OR in this system. However, the presence of martensitic “\(\omega\)” phase significantly modifies the morphology of \(\alpha\) phase in the grain-interior. Despite the external complications that are present in the material, it is expected that the Burgers-OR and grain-boundary parameters would affect the morphology of GB\(\alpha\) in this system.

Figure 116 shows two sets of EBSD data collected at different grain-boundaries and triple points. The refined size-distribution of \(\alpha\) phase in the grain-interior precluded its detection and the crystallography of different \(\beta\)-grains as well as GB\(\alpha\) was revealed. It was found, that in case of continuous GB\(\alpha\) precipitates, the constituent small crystallographic pockets produce nearly same crystallographic variants. Even for the ‘discrete’ GB\(\alpha\) phase, the production of a similar variant was generally found. In a small number of cases, generation of multiple variants has been detected especially in case of ‘discrete’ GB\(\alpha\) phase. The resolution limit of the EBSD data cannot resolve small differences in the crystallography of small pockets of GB\(\alpha\) in morphologically ‘continuous’ precipitates. With regard to the variant-selection, any decisive trend for the contribution of misorientation angle/axis could not be established. In order to determine the role of the GB plane, the methodology described in chapter 5 has been adopted. Initially, the crystallographic orientation of GB planes was determined relative to the
parent β grain that produced a Burgers-OR with GBα. Subsequently, it was transformed to the reference frame of respective variant selection. Finally, in order to bring all GB planes onto the same platform, another transformation was performed in order to express GB plane in the reference frame of a common variant.

The resulting plot (Figure 117) shows that morphologically ‘continuous’ precipitates were produced within 45° of the habit plane. As expected, the ‘discrete’ morphology is produced for GB planes orienting close to $[\overline{1}1\overline{1}]_\beta \parallel [\overline{2}1\overline{0}]_\alpha$ of the Burgers-OR in a majority of cases. This behavior is similar to the behavior observed for the slow-cooled microstructures. However, in this case a significantly higher population of GBα precipitated at low angle grain-boundaries. At such boundaries, even for the GB plane oriented towards the broad face of the Burgers-OR, ‘discrete’ morphologies of GBα are produced in some of the cases. These observations suggest that in addition to the GB plane, low grain-boundary energy or low diffusivity can contribute to the production of ‘discrete’ morphologies. For the high angle grain-boundaries, there appeared to be no preference for a particular range of misorientation angles that produce a ‘discrete’ GBα phase. As for the slow-cooled microstructures, the orientation of GB plane relative to the variant selection directly controls the morphology of GBα. Contrary to the observations made for the slow cooled microstructures, it was not observed that the closeness of $<111>$ and $<101>$ poles of the adjacent grains on variant selection and morphology was important.
6.4.4 Implications on Thickening Characteristics of GBα in Ti-550

As noted in chapter 5, the role of misorientation angle/axis on the morphology of GBα could not be isolated in the well-developed microstructure of Ti-550 because it was difficult to find the grain-boundaries where GBα precipitated preferentially. Therefore, the findings of this work regarding the contribution of misorientation angle and axis on the preferred grain-boundaries in Ti-5553 have been implemented. Both the Ti-550 and Ti-5553 alloys have been subjected to similar thermo-mechanical processing conditions. The approach that has been adopted to indirectly determine this aspect is as follows: average misorientation among the closest <111> and <110> of adjacent grains were determined and correlated with both thickness of GBα and variant selection. Results indicated that in ~65-70% cases, closeness of these poles contributed to the variant selection. On the other hand, the GB plane preferred to orient nearly perpendicular to [1\(\overline{1}\)1], \([2\overline{1}\overline{1}\overline{0}]_\alpha\] in ~50% of the cases.

As shown in Figure 118, the average thickness of GBα has been plotted with increasing misorientations between <101> and <111> poles of adjacent grains. A distinction amongst different misorientation angles has been made by color-coding of GBα. Clearly, for each of the ranges of misorientation angles, the average thickness was lower for higher angles between these poles. These results confirm the importance of misorientation angle/axis on the early nucleation of GBα in Ti-550 alloy. In some of the cases, the production of thick GBα close to the broad-face (Figure 119) also corresponded to the presence of close <111> and/or <110> poles of adjacent grains,
which makes it difficult to judge the relative contributions of GB plane and misorientation angle/axis. Therefore, in order to isolate the role of each of these factors, two possible kinds of cases needed to be filtered out and tested. These are,

(a) Variation in thickness of GB\(\alpha\) upon a change in the orientation of GB plane
(b) GB\(\alpha\) with close poles of \(<110>\) and \(<111>\) of neighboring grains, and oriented away from the broad-face.

Figure 119 highlights (by red circles) some cases that belong to both of these scenarios. All these cases produce low angles between closest poles of interest. Therefore, it is expected that these GB\(\alpha\) precipitate early during the transformation. However, it is clear that in all of these cases, the resulting thickness is significantly smaller as compared to those oriented close to the broad face. This confirms that the GB plane has played an important role in their thickening characteristics. Another example is shown in Figure 119 for two GB\(\alpha\) (A and B) precipitates present on the same grain-boundary. Their morphologies and locations have been shown in Figure 120. Evidently, there is a significant variation in the thickness of GB\(\alpha\). Also, the fact that both GB\(\alpha\) precipitates choose the same crystallographic variant makes this an ideal candidate for comparison. As expected, a reduction in the thickness of GB\(\alpha\) is observed in cases where the GB plane oriented away from the broad (location B).

These examples emphasize the fact that the thickening characteristics in Ti-550 alloy are influenced by both misorientation angle/axis and the orientation of the GB plane relative to the variant selection. These results are essentially an extension of the results obtained for the Ti-5553 alloys, which indicate the similarity of the diffusional
transformation characteristics in titanium alloys, at least in the compositional range of Ti-550 and Ti-5553 alloys.

6.5. Summary

In the present study, the role of grain-boundary parameters on the early growth stages of GBα has been evaluated in a Ti-5553 alloy. A similar exercise has been performed for an entirely different heat-treatment, in which material was water-quenched from the β-annealing temperature and subsequently heated at 5°C/min to 650°C and finally water-quenched. The major outcomes of this work are:

- Early nucleation occurs for misorientation angles > ~20°.
- Misorientation angle/axis dominates early nucleation and growth as well as crystallographic variant selection of GBα precipitates.
- The presence of closely oriented <110> and <111> poles of the adjacent β grains are the preferred sites for the early precipitation.
- These close poles also contribute to the crystallographic variant selection and significantly short-list the allowed variants that GBα can adopt.
- The cases where the GB plane contributes more to the formation of GBα, it tends to orient nearly perpendicular to \([1 \bar{1} 1]_β \parallel [2 \bar{1} 0]_α\) of the Burgers-OR.
- The interaction of GB plane with variant selection controls the morphology of GBα, where continuous precipitates get produced when a GB plane orients
perpendicular to \([1\bar{1}1]_\beta \parallel [2\bar{1}0]_\alpha\), and discrete precipitates tend to form at significant deviations from this orientation.

- For the \(\beta\)-annealed, water-quenched and heated at 5°C/min to 650°C and water-quenched sample, both misorientation angle and GB plane control the morphology. Discrete GB\(\alpha\) gets produced at low angle grain-boundaries and for the orientations of GB plane towards \([1\bar{1}1]_\beta \parallel [2\bar{1}0]_\alpha\) of the selected variant.

- For Ti-550 alloy, in addition to the interaction of GB plane with variant selection (as discussed in chapter-5), misorientation angle/axis has an important contribution.
Figures

Figure 91: Micrographs show the microstructural evolution of Ti-5553 alloy soaked at (a) 825°C, (b) 800°C, (c) 775°C and (d) 750°C after β-annealing at 1000°C.
Figure 92: At 825°C, the formation of GBα occurred at isolated grain-boundaries.
Figure 93: Micrographs show (a) the formation of GBα at certain grain-boundaries. In addition, the production of continuous’ and discrete morphologies, shown by ‘a’ and ‘b’ is also observed in micrograph (b).
Figure 94: At 775°C, there is a large increase in the volume fraction of $\alpha$ phase. Moreover, grain-boundaries get decorated by GB$_\alpha$ and the formation of Widmanstätten $\alpha$ plates precedes the precipitation of $\alpha$ at certain grain-boundaries.
Figure 95: At 750°C, there is a higher fraction of Widmanstätten $\alpha$ plates in grain-interior and a complete saturation of grain-boundaries by GB$\alpha$.

Figure 96: Micrographs show the microstructure of quenched and aged sample. Clearly, the morphology of GB$\alpha$ precipitates is quite distinct at different boundaries.
Figure 97: Micrographs show the presence of GB$\alpha$ at certain grain-boundaries.
Figure 98: Plot shows the distribution of the fraction GBα (total ~40) precipitates with the indicated ranges of misorientation angles (ω). Here, (1) $0^\circ \leq \omega < 10^\circ$, (2) $10^\circ \leq \omega < 20^\circ$, (3) $30^\circ \leq \omega < 40^\circ$, (4) $40^\circ \leq \omega < 50^\circ$ and (5) $50^\circ \leq \omega < 62^\circ$. GBα apparently has significantly higher fractions at high angle grain boundaries and achieves a maximum between $40^\circ \leq \omega < 50^\circ$. 
Figure 99: Schematic shows the distribution of disorientation angles for random microstructures.
Figure 100: Pole-figures show the formation of a continuous layer GBα that produced a near Burgers-OR with both grains (misoriented by 60°/⟨110⟩). Here, blue circles correspond to the OR relative to blue grain and red circle corresponds to the yellow grain.

Figure 101: The early precipitation of GBα preferentially occurred for (a) close ⟨101⟩ poles (shown by the blue circle) and (b) close ⟨111⟩ poles of the adjacent β grains.
Figure 102: Poles of $<101>$ and $<111>$ of adjacent $\beta$ grains that contributed to the early production of GB$\alpha$ tend to cluster in different regimes of misorientation angles.

Figure 103: Plot shows the higher distribution of the closeness of $<111>$ and $<101>$ poles at low angle grain-boundaries for the hypothetical case of the equal probabilities of all disorientation angles.
Figure 104: Plots show the (a) normalized frequency and (b) actual distribution of minimum angles (≤ 10°) between <101> poles (shown in red) of adjacent grains, and between <111> poles (shown in blue) for a random microstructure. Here, black curve in plot (a) shows the distribution of disorientation angles for a random microstructure.
Figure 105: Micrograph shows the presence of multiple variants of GB$\gamma$: (i) to (iv), present along the same grain-boundary. Here the misorientation between grain-A and grain-B is 0.4 degrees. Thus variant (iv) is also nearly comparable to other variants.
Figure 106: Pole figures represent the production of Burgers-OR of different variants on the same grain-boundary (Figure 105) that has misorientation angle ~ 27.5°/111> i.e. co-incidence site lattice (CSL) of 13b.
Figure 107: Pole-figures and micrographs show the examples of GB\(\alpha\) where the close \(<111>\) (shown by red circles) and close \(<101>\) (shown by black circles) of adjacent grains did not contribute to the variant selection. Selected variants are indicated by the red and black arrows.
Figure 108: Stereographic projection shows that the closeness of <111> poles of adjacent β grains leads to a short-listing of allowed variants to six from 24, as shown by red and blue arrows. The blue circle indicates the variant selected by GBₙ.
Figure 109: Micrographs show the production of, (a) continuous and (b) discrete morphologies of GB\(\alpha\) during the early growth stages.
Figure 110: Micrograph shows the approach used to produce FIB trenches nearly perpendicular to the local orientation of GB planes to account for the grain-boundary reorientation.
Figure 111: Stereographic projection shows the orientation of GB planes relative to the common Burgers-OR. Evidently, discrete precipitates tend to orient towards $[\bar{1}\bar{1}1]_p \parallel [2\bar{1}0]_\gamma$ of Burgers-OR, while most of the continuous GB$_\alpha$ precipitates orient nearly perpendicular to this direction.
Figure 112: Cases where misorientation angle/axis does not play an important role, GB plane preferred to orient nearly perpendicular to $[1 \bar{1} 1]_\beta \parallel [2 \bar{1} 0]_\alpha$. 
Figure 113: Stereographic projections show the short-listed GB plane orientations when the misorientation angle/axis dominates the variant selection. In this particular case, it forced (a) GB plane to orient towards \([1 \bar{1} 1]_\beta \parallel [2 \bar{1} 0]_\alpha\) and produce a discrete morphology and vice-versa for (b).
Figure 114: Schematic pictorially shows the influence of GB plane relative to the variant selection on continuous and discrete morphologies of GBα. GB plane causes GBα to grow in a different direction away from its ideal morphology (decided by the variant selection) and reorients significantly to accommodate its growth.
Figure 115: Micrographs show the formation of (a) discrete and (b) continuous GB\(\alpha\) precipitates at different grain-boundaries in the \(\beta\)-annealed, water-quenched and aged sample.
Figure 116: Micrographs show examples of EBSD data collected on the β-annealed, quenched and aged sample.
Figure 117: Stereographic projection shows the formation of discrete GB\(\alpha\) precipitates for orientations of GB plane towards \([1\bar{1}1]_\beta \parallel [\bar{2}1\bar{0}]_\alpha\) of Burgers-OR.
Figure 118: A high thickness of GB$\alpha$ was produced for a low angular distance between the closest $<110>$ poles and/or $<111>$ poles of adjacent $\beta$-grains at different ranges of misorientation angles in Ti-550 alloy.
Figure 119: In Ti-550 alloy, the low thickness of GB$_\alpha$ close to the broad-face (indicated by black arrows) corresponds to a probable precipitation at a high under-cooling. GB$_\alpha$ highlighted by circles away from the broad face probably undergo early nucleation yet produced significantly thin precipitates.
Figure 120: Micrographs show a change in the thickness of \( \text{GB}_\alpha \) from location A and B lying on the same grain-boundary for Ti-550, indicated in Figure 119. Clearly the orientations of GB plane and the thickness of \( \text{GB}_\alpha \) at locations A and B are significantly different.
Table 6: Table enlists details of grain-boundary parameters corresponding to GBα considered for the heat-treatment (b) in Ti-5553.

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Table 7: Table summarizes the details of grain-boundaries that have been studied for the sample that has been β-annealed, water-quenched and heated at 5°C/min to 650°C and finally aged.

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Chapter 7
Analysis of Interfacial Structure between Allotriomorphic $\alpha$ and $\beta$ in $\beta$-Processed Ti-550 Alloy

7.1 Abstract

In titanium alloys, a low energy configuration between $\beta$ and $\alpha$ phases is attained by the production of Burgers orientation relationship (OR). In the grain-interior, this relationship decides the major growth direction and morphology of $\alpha$ phase in the $\beta$-matrix. In addition, a combined effect of Burgers-OR and lattice parameters determines the interfacial structure between these two phases. In case of allotriomorphic or grain-boundary $\alpha$ (GB$\alpha$), the presence of grain-boundaries generally forces this phase to grow in a different direction away from its ideal morphology and also modifies the interfacial structure. In this chapter, transmission electron microscopy (TEM) studies have been conducted to characterize various defects present on the interface of GB$\alpha$ and adjacent $\beta$-grain that produced an OR for different crystallographic orientations of the GB plane. Results indicate that the GB$\alpha$-$\beta$ interface underwent a faceting. It contributed to a variation in the defect-structure. A change in the inclination of GB plane relative to the Burgers-OR produced new types of misfit dislocations/ledges, which are significantly different from the expected interfacial structure as defined by the OR. These observations probably indicate an accommodation of volumetric misfit strain by the GB plane.
7.2 Introduction

The formation of lath shaped morphology on Widmanstätten α plates in α/β-titanium alloys is caused by Burgers-OR and lattice parameters of α and β phases in titanium alloys [35]. However, allotriomorphic or grain-boundary α (GBα) precipitated at different grain-boundaries does not take this ideal morphology. The presence of grain-boundary modifies its growth characteristics. As it was observed in the previous chapter, GBα wets the grain-boundaries and preferentially grows along them. In this process, the reorientation of the GB plane occurs and in general, the interaction of GB parameters and variant selection controls the morphology GBα. It is expected that this deviation from the ideal morphology would alter the interfacial structure by accommodating the elastic misfit strain. In this chapter, the evolution of interfacial structure has been quantified for various orientations of the GB plane with respect to the crystallographic variant of the corresponding GBα.

With reference to the observations made in chapter-5, three important cases have been selected for the TEM analysis. These cases have been shown in the stereographic projection produced in the reference frame of Burgers-OR (Figure 121a) and the corresponding schematic with respect to the ideal morphology of α phase is also shown (Figure 121b). These cases have been chosen because they do not produce a deviation from Burger-OR with one of the adjacent grains. More importantly, they represent nearly the extreme cases relative to the Burgers-OR. While scenario (i) brings the GB plane close to the broad-face, scenarios (ii) and (iii) orient the GB plane close to
(\text{1\overline{1}0})_\beta \parallel (0001)_\alpha \text{ and } [1\overline{1}T]_\beta \parallel [2\overline{1}\overline{1}T]_\alpha \text{, respectively. As a base-line, the interfacial structure of Widmanstätten } \alpha \text{ platelet has also been studied. The location of this interface would lie along the broad face or } [1\overline{1}T]_\beta \text{ in Figure 121.}

7.3 Experimental Procedure

A forged sample of Ti-550 (Ti–4(wt%)Al–4Mo–2Sn–0.5Si) alloy was \( \beta \)-processed (\( \beta \)-annealed at 1030°C for 90 minutes and slow-cooled to room temperature in the furnace in an inert atmosphere) to produce a colony microstructure. Subsequently, it was sectioned and carefully polished using standard metallographic methods for the microstructural characterization. Next, an FEI DualBeam™ Helios focused ion beam (FIB) microscope was used to produce site-specific sections at different grain-boundaries. The orientation of these FIB trenches was kept nearly perpendicular to the traces of grain-boundaries that intersect the polished specimen surface. In this way, the true three-dimensional morphologies and thicknesses of different GB\( \alpha \) precipitates were revealed. The secondary electron beam oriented at 52° relative to the ion beam was used to image the sectioned regions. The details of the experimental methodology have been described in detail in chapters 4 and 5.

For the analysis of the interfacial structure using a TEM, an Helios DualBeam™ FIB microscope was again used to produce site-specific thin-foils to achieve an electron transparency. To determine the prior-\( \beta \) grain that produced a near Burgers-OR with GB\( \alpha \), standard diffraction or Kikuchi pattern techniques have been utilized. The interfacial
structure was revealed by orienting the sample along different \( g \) vectors. Images were recorded in the bright-field, dark-field and weak-beam modes at suitable magnifications for a further analysis. These images were collected at a known camera length of 500 mm using Phillips CM200T conventional transmission electron microscope.

7.4 Results and Discussion

Figure 122 shows the morphology of all three GB\( \alpha \) precipitates relative to the surface of the specimen and the adjacent prior-\( \beta \) grain that produced a Burgers-OR with them. Figure 123 shows the corresponding micrographs produced using TEM in the bright-field mode. These micrographs clearly indicate that in general, a continuous thick layer of \( \beta \) phase was not present over the entire length of the interface. A variation in the curvature of the interface at different locations was observed. Therefore, characterization of the interfacial structure has been carried out at representative regions as highlighted in the images because they locally offer a relatively large interfacial area of GB\( \alpha \) and a thick layer of \( \beta \). These regions also orient relatively close to the average orientations calculated using the EBSD based methodology. A visual comparison of the interfaces for the location (iii) with those for (i) and (ii) suggests that for the later two cases, the trace of GB plane macroscopically orient close (with some angular variation) to the broad face of the corresponding Widmanstätten \( \alpha \) platelets on the ‘Burgers’ side. In contrast, it oriented nearly perpendicular to it at location (iii), which also matches with the predictions made in the stereographic projection plot shown in Figure 121a.
In this work, primarily the Burgers vectors ‘\(b\)’ and the line directions of various defects (dislocations/ledges) present at the interfaces of GB\(\alpha\) and \(\beta\) have been determined to understand their edge/screw/mixed characters. The methodology to determine the line-directions of the defects has been described in chapter-5, which essentially involves determining the geometry of the projected orientations of various defects at three (at least two) major crystallographic zones and known diffraction vectors. The pole of the great-circle produced by these three projections constitutes the actual line direction of the defects.

The Burgers vector ‘\(b\)’ of the dislocations are determined using the concept that for a particular set of diffraction vectors ‘\(g\)’, its scalar product (or the dot product) with ‘\(b\)’ would result in a dislocation-invisibility. In particular,

For screw dislocations, invisibility criteria: \(g \cdot b = 0\)

For edge dislocations, invisibility criteria: \(g \cdot b = 0\) and \(g \cdot (b \times u) = 0\)

Details of the overall methodology for a complete characterization of defects have been described elsewhere [93].

7.4.1 Widmanstätten \(\alpha-\beta\) Interface

Figure 124 shows the bright field image of Widmanstätten \(\alpha\) platelet and adjacent thick layer of \(\beta\)-phase. The dark-field images produced under two-beam conditions for \([0002]_\alpha\), \([\bar{T}010]_\alpha\) and \([2\bar{T} \bar{T}0]_\alpha\) \(g\) vectors respectively show the invisibility of highlighted defect in the later two cases (Figure 125). This defect is uniformly spaced and
covers the entire interfacial area. Apparently, the Burgers vector of this defect is of the type: ‘c’ or $[0001]_\alpha$. The line direction of this defect was found to be close to $[1\bar{T}1]_\beta || [2\bar{T}\bar{T}0]_\alpha$, which shows that these defects have an edge character. With reference to the analysis performed in chapter-5, it is known that this interface represents the broad face or $[1\bar{T}1]_\beta$ direction as indicated in Figure 121. Previous studies have discussed that these defects discussed above are the misfit-ledges and they cover the broad- and edge-faces of $\alpha$ phase (Figure 121b). High resolution TEM analysis has proposed the exact Burgers vectors of these edge type defects as $(\frac{c}{2})[0001]_\alpha [108]$. 

In addition, multiple sets of wavy defects have been observed, which have been found to be of both ‘c’ and ‘c+a’ types. These defects in-general posses a mixed character and do not contribute to the structural component of the interfacial structure. The ‘a’ type structural ledges shown in chapter-2 have not been observed in technique due to the small Burgers vector of $(\frac{a}{12})[2\bar{T}\bar{T}0]_\alpha [108]$, which makes ‘g,b’ value close to zero. In addition, the inter-ledge spacing of these ledges is too small to be resolved in a conventional TEM. Furuhara et. al. (1995) has utilized high-resolution TEM for this purpose.

7.4.2 GB$\alpha$ (i)-$\beta$ Interface

With reference to Figure 121, this GB$\alpha$ orients close to the broad face of the Burgers-OR. A number of defects that get produce because of the faceting of the
interface have been indicated in Figure 126. Interestingly, in between the regions consisting of defects, relatively planar facets were present at multiple locations. A deviation from this configuration introduced defects in the interface. The TEM-foil was tilted by nearly $14^\circ$ from $[1\bar{T}1]_\beta \parallel [2\bar{T}0]_\alpha$ towards the invariant line to make this interface nearly edge-on relative to the beam. Therefore, this surface oriented nearly $14^\circ$ away (towards the invariant line) from $[01\bar{T}1]_\alpha$ (Figure 127).

Table 8: Table shows diffracting vectors needed to produce invisibilities for all six defects, and also enlists the resulting Burgers vectors.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\mathbf{g}$ vectors</th>
<th>Type of Burgers vector $(\mathbf{b})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Visibility</td>
<td>Invisibility</td>
</tr>
<tr>
<td>A</td>
<td>$[0002]_\alpha$</td>
<td>$[10\bar{T}1]_\alpha$</td>
</tr>
<tr>
<td>B</td>
<td>$[0\bar{T}10]_\alpha$</td>
<td>$[11\bar{2}0]_\alpha$</td>
</tr>
<tr>
<td>C</td>
<td>$[0002]_\alpha$</td>
<td>$[10\bar{T}1]_\alpha$</td>
</tr>
<tr>
<td>D</td>
<td>$[0\bar{T}10]_\alpha$</td>
<td>$[11\bar{2}0]_\alpha$</td>
</tr>
<tr>
<td>E</td>
<td>$[0\bar{T}10]_\alpha$</td>
<td>$[0002]_\alpha$</td>
</tr>
<tr>
<td>F</td>
<td>$[0\bar{T}10]_\alpha$</td>
<td>$[11\bar{2}0]_\alpha$</td>
</tr>
</tbody>
</table>

Six kinds of defects (A-F) have been identified, where ‘A’ and ‘B’, ‘C’ and ‘D’, ‘E’ and ‘F’ respectively lie on the same interfaces. Figure 128 and Figure 129 show the dark-field micrographs produced for various two-beam conditions. A summary of visibilities and invisibilities of these defects for different diffraction conditions has been given in
Upon analysis, A and C defects have found to be of type ‘c’ while B and D defects are of type ‘a’. Both these defects accommodate a change in the orientation of the interface. The formation of defect F is not a geometrical necessity and is most likely a growth ledge. This defect is of the type ‘a’. Finally, defect E lies on the surface that is oriented along a different direction relative to A, B and B, D defects; this defect is of \([1\bar{1}01]_\alpha\) type.

The line directions of those defects that contribute to the structural aspects of the interfaces have also been determined. An example of the approach based on the stereographic projection to determine the line direction is shown in Figure 130. Results show that defects A and C have predominantly edge character because these are ‘c’ type defects and the line direction of their line direction is close to \([4\bar{1}31]_\alpha\), which is around 84° away from \([0001]_{\alpha}\) (Figure 130a). Defects B and D have been found to have a mixed character. Finally, as shown in Figure 130b, Defect E has line direction very close to \([1\bar{1}1]_\beta \|[2\bar{1}0]_{\alpha}\), which gives a mixed character to it because the Burgers vector of these defects is: \(k[1\bar{1}01]_{\alpha}\).

### 7.4.3 GB\(\alpha\) (ii) – β Interface

Figure 131 shows the presence of two types of defects at the interface of GB\(\alpha\) (ii) and β. Defect B exhibits a more sensitive response to a variation in the orientation of GB plane as compared to defect A. Defect A is closely spaced over the entire extent of the interface. Figure 132 shows the dark-field micrographs at different two-beam conditions:
[1\bar{T}01]_\alpha and [0002]_\alpha$. In both cases, both defects are visible. Defect A exhibits invisibility for diffracting vectors: $[2\bar{T}\bar{T}0]_\alpha$ and $[1\bar{T}00]_\alpha$. While defect B becomes invisible for g vectors: $[01\bar{T}\bar{T}]_\alpha$ and $[2\bar{T}\bar{T}0]_\alpha$. (Figure 133). Therefore the Burgers vectors of A and B are of types $[0001]_\alpha$ and $[01\bar{T}2]_\alpha$ respectively.

The line directions of these defects have been plotted in Figure 134, which clearly shows the mixed nature of both of the defects. Defect A maintains its spacing and defect-structure even with a change in the orientation of the interface while the projected spacing of defect B undergoes a change in this process.

7.4.4 GB\(\alpha\) (iii) – β Interface

This allotriomorphic \(\alpha\) precipitate is produced at the grain-boundary that is oriented more towards $[1\bar{T}1]_\rho \parallel [2\bar{T}\bar{T}0]_\alpha$ of the Burgers-OR. Figure 135 shows the presence of three-types of defects at the interface of GB\(\alpha\) and β phase. Defects A and B produced a uniform spacing over the entire surface. While, defect C produces a non-uniform line direction that varies with the inclination of the interface. The two-beam dark-field images produced for diffracting vectors: (a) $[0002]_\alpha$ and (b) $[\bar{T}10\bar{T}]_\alpha$ show the presence of all three defects (Figure 136). Defects A and C become invisible for $[1\bar{T}00]_\alpha$ and $[1\bar{T}10]_\alpha$ (Figure 137), which makes their Burgers vector of the type ‘c’ or $[0001]_\alpha$. 

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Finally defect B becomes invisible for $[2\overline{1}0]_\alpha$ and $[01\overline{2}]_\alpha$ (Figure 138). Therefore the Burgers vector for this defect becomes $[01\overline{1}]_\alpha$.

The line directions of each of these defects are shown in Figure 139, which shows the mixed character of both defects.

It is interesting to note that ‘c’ type defects are present at all orientations of GB planes considered in the present work. They generally produce a mixed character, which is different from the observations made at the interface of Widmanstätten $\alpha$ and $\beta$. These results are similar to ones observed by Furuhara et. al. (1991). A variation in the orientation of an interface is accommodated by an additional set of defects. These defects have found to be of all ‘a’, ‘c+a’ and ‘c’ types. A faceting of this interface has been observed in all cases. The presence of these facets probably indicate the existence of local saddle points in interfacial energy curve of Burgers-OR.

At this juncture, a quantitative explanation and prediction of the variation in the defect structure at different orientations of GB planes are difficult. An analysis of more cases is needed to understand the effect of GB parameters. However, the results of this work can be used to understand the dislocation content and therefore determining the energy of GB$\alpha$ and $\beta$ interface, which would be useful in modeling studies. These results could also be used in simulation studies to understand the difference in misfit strain as compared to that for Widmanstätten $\alpha$.

There are some major shortcomings of the present work. It is known that GB$\alpha$ generally exhibits some deviation from the exact Burgers-OR. In this study as well, this behavior has been frequently observed in a number of cases. Nevertheless for the cases
discussed in this chapter, a care has been taken to consider only those grain-boundaries that do not deviate from the orientation relationship. For more general cases however, it is necessary to consider all GB parameters to quantify their effect on interfacial structure. The results obtained in this study do not readily explain as how does the misfit strain get accommodated while maintaining a Burgers-OR.

Finally, the magnitudes of Burgers vectors have not been determined. It is expected that those misfit dislocations that accommodate the variation of orientation of GB plane have magnitude same as those of corresponding matrix dislocations. However, closely spaced defects that are present at all interfaces and are independent from their change in orientation could produce fractional magnitudes. More studies are required to determine their magnitudes.

7.5 Summary

This chapter aims to report a variation in the defect-structure of the interface between GBα and β phase for different orientations of GB planes relative to the selected variant Burgers-OR by GBα. The interface of Widmanstätten α and β phases consisted of ‘c’ type defects that have an edge character. The presence of GB plane modifies the interfacial structure. The main results of this work are:

- ‘c’ type defects have been observed for all the orientations of GB planes considered in this work. They produce edge or mixed character. Screw type defects have not been observed.
Certain defects accommodate a variation in the orientation as well as faceting of the interface. Depending upon the orientation of GB plane they have found to be of ‘a’, ‘c+a’ and ‘c’ types. These defects generally change their spacing and line directions at different locations along the interface.

Other types of defects that are found on these interfaces maintain their spacing and line directions over the entire surface and constitute a structural component of the interfacial structure. These defects generally are of [0001] and \(<01\overline{1}\overline{1}>\) types.
Figures

Figure 121: (a) Schematics show three different cases considered for the analysis of interfacial structure for the GB planes oriented towards, (i) broad-face, (ii) side face and (iii) edge-face, as indicated in (b) by blue lines (corresponding to the GB plane normals).
Figure 122: Secondary electron micrographs show the morphologies of GBα analyzed in this study. Here (i), (ii) and (iii) correspond to the locations specified in Figure 121a. The arrows in the images indicate the prior-β grains that produced a Burgers-OR.
Figure 123: Low magnification bright-field TEM micrograph corresponding to (i), (ii) and (iii) locations in Figure 121 indicate the regions where analysis has been performed.
Figure 124: Micrograph shows the region chosen for analyzing Widmanstätten $\alpha$-$\beta$ interface.
Figure 125: Dark-field micrographs show the interfacial structure of Widmanstätten $\alpha$ platelets and adjacent $\beta$ phase for (a) [0002]$_{\alpha}$, (b) [1010]$_{\alpha}$ and (c) [2110]$_{\alpha}$ g vectors respectively.
Figure 126: Dark-field TEM micrograph shows the presence of various defects (A-F) present at the interface of GBα (i) and β-matrix. There also exists a relatively planar region between the defects ‘A-B’ and ‘C-D’.
Figure 127: Micrograph produced close to \([1\overline{1}1]_\beta \parallel [2\overline{1}\overline{1}0]_\alpha\) shows the orientation of the facets of the interface for GB\(\alpha\) (i).
Figure 128: Dark-field micrographs produced under the two-beam conditions corresponding to diffraction vectors of (a) $[0002]_\alpha$, (b) $[11\bar{2}0]_\alpha$ and (c) $[0\bar{1}10]_\alpha$ show the visibilities/invisibilities of various defects.
Figure 129: Dark field micrograph for the diffraction vector of $[10\overline{1}1]_\alpha$ shows the invisibilities of defects ‘B’, ‘D’, ‘E’ and ‘F’.
Figure 130: Stereographic projections indicate the line directions of (a) defect A and (b) defect E.
Figure 131: Micrograph shows the presence of two types of interfacial dislocations A and B at \(\text{GB}_\alpha\) (ii) – \(\beta\) interface.
Figure 132: Micrographs show the visibility of both interfacial defects for g vectors: (a) \( [1 \bar{1} 01]_\alpha \) and (b) \( [0002]_\alpha \) respectively.
Figure 133: Defects A and B become invisible for $g$ vectors: (a) $[01\bar{T}1]_u$ and (b) $[2\bar{T}0]_u$.

and for (b) $[2\bar{T}0]_u$ and (c) $[1\bar{T}00]_u$ respectively.
Figure 134: Stereographic projections show the line directions of defects A and B present in GB\(\alpha\) (ii)-\(\beta\) interface.
Figure 135: Micrograph shows three types of defects present at the GBα (iii) - β interface.
Figure 136: Micrographs show the presence of all three types of interfacial defects for $\mathbf{g}$ vectors: (a) $[0002]_a$ and (b) $[110\overline{1}]_a$.
Figure 137: Micrographs show the invisibilities of defects ‘A’ and ‘C’ for g vectors: (a) \([\bar{1}00]_\alpha\) and (b) \([1210]_\alpha\).
Figure 138: Micrographs show the invisibility of defect ‘A’ for \( \mathbf{g} \) vectors: (a) \([2\bar{1}\bar{1}0]_\alpha\)
and (b) \([01\bar{1}2]_\alpha\) .
Figure 139: Plots show line directions of defects A and B at GBα (iii)-β interface.
Chapter 8
Summary and Future Work

In this work, morphology, variant selection and the interfacial structure of allotriomorphic $\alpha$ has been studied with respect to the adjacent $\beta$ grain that established a Burgers orientation relationship with it. Following are the main conclusions of this study:

In chapter-4, two methods to determine the crystallographic orientation of an interface relative to the parent phase have been developed. A combination of EBSD and dual beam FIB has been utilized in both of the methods. Their accuracy and versatility have been confirmed by utilizing well-established crystallographic characteristics of twins present in cubic and hexagonal systems. The requirements of sample preparation in these methods are significantly simpler relative to the TEM based approaches. These methods have been subsequently applied to evaluate the role of GB parameters on allotriomorphic phase transformations in Ti-550 and Ti-5553 alloy systems in subsequent chapters.

In chapter-5, a variation in the thickness of GB$\alpha$ precipitates at different grain-boundaries has been quantified relative to the GB parameters for Ti-550 alloy. An important and interesting outcome of this study is that in case of titanium alloys, a significant thickening of GB$\alpha$ occurs in the adjacent $\beta$ grain that produced a Burgers-OR. In other words, an appreciable growth of an allotriomorphic precipitate occurs in the parent grain that produced a semi-coherent interface with it.
It has been determined that two conditions are needed to produce a thick allotriomorphic \( \alpha \) that involve GB parameters: GB plane, misorientation angle and misorientation axis, and variant selection:

- **Condition-1**: An early nucleation of GB\( \alpha \), which is mainly controlled by misorientation angle and axis.

- **Condition-2**: The orientation of the GB plane close to the habit plane (or broad face) of the selected crystallographic variant of GB\( \alpha \).

For the special cases in which GB\( \alpha \) produces a near Burgers-OR with both of the adjacent grains, thin precipitates are produced if the GB plane orients away from the habit planes of both of the variants of the orientation relationship. The presence of any other scenario leads to the formation of thick precipitates.

In chapter-6, the early growth stages of GB\( \alpha \) have been studied in Ti-5553 alloy. Results indicate that both early nucleation and growth and crystallographic variant selection are primarily controlled by the misorientation angle and axis. Specifically, grain-boundaries that produce close \( <101> \) and \( <111> \) poles of adjacent \( \beta \) grains at high misorientation angles (\( \geq 20^\circ \)) are the preferred nucleation sites. These close poles also contribute to the variant selection in \( \sim 85\% \) cases. This condition appreciably short-lists the allowed variant that GB\( \alpha \) can adopt. The orientation of the GB plane relative to the Burgers-OR controls the morphology; a discrete morphology is achieved when the GB plane orients towards \( [1\bar{1}1]_\beta \) \( \lbrack 2\bar{1}0 \rbrack_\alpha \) of the Burgers-OR. This direction lies nearly perpendicular to the habit plane of the Burgers-OR. A continuous precipitate is produced when the GB plane orients nearly perpendicular to this direction. Misorientation
angle/axis exercises an indirect control on this morphology through the variant selection. A comparison of the findings of this work with previous studies indicates that thermo-mechanical processing can alter the relative influence of misorientation angle/axis and GB plane.

Even in the β-annealed, water-quenched and slow-heated sample, a similar contribution of the GB plane and the variant selection on morphology has been noted. In this case the precipitation of GBα was found to occur at low-angle grain-boundaries as well, but a discrete morphology was produced in most of such cases. Interestingly, EBSD data indicated that a small angular deviation in the variant selection occurred along the grain-boundaries, which is contributed by the fact that these grain-boundaries did not re-orient during the phase transformation.

However, in both chapters 5 and 6 the contribution of the β-grain that produced an irrational relationship with GBα has not been considered. It is known that the morphology and variant selection of GBα get affected by both adjacent grains. It is therefore important to develop a methodology to quantify this effect. In addition, GBα does not generally produce an exact Burgers-OR with any of the adjacent grains. The effect of this deviation on the evolution of GBα needs to be quantified. Another major factor that has not been considered in the present work is the contribution of the diffusion of various chemical species during the phase transformation, especially during the nucleation and early growth stage. The diffusion of these species is known to be the rate controlling step. With regard to variant selection and early nucleation, the exact
mechanism of role of the GB plane and the importance of the close \( \langle 101 \rangle \) and \( \langle 111 \rangle \) poles of the adjacent grains are not well understood.

In chapter-7, the interfacial structure between GB\( \alpha \) and adjacent \( \beta \) grain (that established a Burgers-OR) has been evaluated and compared for three orientations of GB planes. These orientations were close to (i) the habit plane, (ii) \((110)_\beta \ | (0001)_\alpha \) and (iii) \([1\overline{1}1]_\beta \ | [2\overline{1}0]_\alpha \) of Burgers-OR. Similar to the observations made in other studies, the interfacial structure between Widmanstätten \( \alpha \) and \( \beta \) consisted of ‘c’ type misfit defects that oriented along \([1\overline{1}1]_\beta \ | [2\overline{1}0]_\alpha \) and thus exhibited an edge character. Structural ledges were not observed using this approach because of the small Burgers vector of these ‘a’ type ledges.

The introduction of the GB plane modified their growth characteristics and the interfacial structure. In general, there are two types of defect structures were produced for all three cases. The first kind was produced to accommodate a variation in the orientation of the interface. These defects were generally of a mixed character and their spacing varied with a change in the orientation of the interface. Other types of defects were present that had significantly smaller spacing and they maintained their structure irrespective of the orientation of the interface. The first kinds of defects were of generally ‘\( <2\overline{1}0> \)’ , ‘\([0001]_\alpha \)’ and ‘\( <10\overline{1}2> \)’ types and second kind of defects were of ‘\([0001]_\alpha \)’ or ‘\( <10\overline{1}2> \)’ types. Interestingly, most of these defects had a mixed character as well. Although the contribution of a variation in the misorientation between
GB₉ and β phase on the interfacial structure has not been evaluated, all the cases considered in this work produced a near Burgers-OR with one of the adjacent grains.

With regard to future efforts, the findings of the present work pave a way for a number of endeavors not only to understand the evolution of this phase but develop processes to manipulate the microstructural evolution. Following efforts can be made in this regard.

- A methodology to account for the contribution of adjacent β grain, which does not produce a Burgers-OR, needs to be developed on both morphology and variant selection.
- The importance of the close <101> and <111> poles of adjacent grains on both early nucleation and variant selection needs to be studied.
- A higher population of close <111> poles of adjacent grains in the range of misorientation angles (θ): 25°≤θ<40°, and the dominance of close <101> poles in 40°≤θ<50° is not understood.
- The presence of multiple variants at a grain-boundary seriously challenges the existing rules of variant selection. More studies are needed in this regard.
- The role of the GB parameters on variant selection in β-annealed, water-quenched and aged microstructure needs further study.
- Grain-boundary engineering studies in order to manipulate ‘continuous’ and ‘discrete’ morphologies of GB₉ need to be performed and the influence of these morphologies on various mechanical properties needs to be investigated.
• The early precipitation of Widmanstätten $\alpha$ close to discrete GB$\alpha$ is an important aspect of the microstructural evolution. In-depth studies are needed to understand this effect.

• With regard to the interfacial structure of GB$\alpha$-$\beta$ interface, the contribution of misorientation angle/axis needs quantification. Also the accommodation of misfit strain by the GB plane also requires further studies.

• A deviation from the exact orientation relationship between GB$\alpha$ and $\beta$ phase could also influence the interfacial structure and morphology, which requires a further investigation.

• Also, determination of the dislocation content of various defects for different orientations of the GB planes would be useful for the modeling studies.
References

16. J. Delfosse, C. Rey and M.H. Mathon, Materials Science 77.
54. E. P. Barry, Masters Thesis; The Ohio State University; 2008.
82. H.J. Bunge, Z. Metallkde. 56(1965) 872.
86. R.E.A. Williams, PhD thesis. The Ohio State University (2010).
96. S. Koduri, V. Dixit J.M. Sosa, P.C. Collins, H.L. Fraser, Unpublished work.