3-DIMENSIONAL ANALYSIS OF MICROSTRUCTURES IN TITANIUM

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This thesis is dedicated to Shri Bhola Nathji Bhagwan.
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Chapter 1 Introduction
Titanium, owing to its great affinity towards oxygen, is relatively costly to produce, especially when compared to other structural materials like steel. This is the main reason that despite having excellent properties like toughness, strength to weight ratio and good corrosion resistance, large scale use of titanium and its alloys has not occurred. There are, however, alloys like the Titanium Low Cost Beta (Ti-LCB) which are cheaper to produce and thus hold a promise for titanium as structural material of the future.

The very wide range of properties that is obtained in metals is primarily due to the different solid-solid phase transformations that occur during thermal/thermo-mechanical treatments. The control and tuning of microstructures, and in turn, other properties, is dependent on our understanding of how the microstructures evolve.

One of the solid state phase transformation products (primary $\alpha$) formed during isothermal treatments in a Ti-LCB alloy is investigated in this project by employing three dimensional (3-D) analysis using serial sectioning, 3-D EBSD and FIB 3-D EBSD. The necessity to study different size scales and characteristics requires multiple methods of analysis. In combination, elemental analysis and Electron Backscatter Diffraction (EBSD) are used to understand the mechanism of formation of the $\alpha$ phase. Special morphological features like “zigzag” morphology are studied. In addition, some aspects of $\omega$ and martensitic phase formation in the alloy are analyzed.

The general characteristics of titanium are presented in Chapter 2 followed by brief overviews of the different phases that are obtained during various thermal treatments in titanium. Primary $\alpha$ is discussed in detail including interfacial aspects, followed by a review and comparison of sympathetic nucleation and interface instability. Chapter 3 gives a theoretical background of the experimental techniques and the experimental procedures followed in this project. Chapter 4 presents results of various analyses of transformed microstructures, including optical microscopy, serial sectioning, 3-D EBSD, Focused Ion Beam (FIB) 3D-EBSD and Wavelength Dispersive Spectrometry (WDS). Also discussed are mechanisms for formation of primary $\alpha$ including interfacial analysis corresponding to zigzag morphology. $\omega$ phase and martensite formation characteristics of the alloy are given at the end of Chapter 4. Chapter 5 outlines the conclusions of the project and some recommendations for future work are given in Chapter 6.
Chapter 2 Background

2.1 General characteristics of titanium

Titanium is a transition metal element, belonging to group IVa, with atomic number 22 and atomic mass of 47.9. The melting point of pure titanium is 1668 °C. It is the fourth most abundant metal in nature, bested only by aluminium, iron and magnesium; ahead of copper, lead and zinc. Overall, titanium is the ninth most abundant element in the earth’s crust, making up about 0.57 wt% of it. This section will describe some of the general characteristics, production methods and possible applications.

2.1.1 Titanium production

Titanium is very reactive with oxygen and forms very strong ionic bonds. This makes extraction of titanium from its oxide ores rather difficult. The first successful attempt to produce industrial scale extra pure titanium was in 1932 by Justin Kroll in Luxemburg. The process, named after him as Kroll process, was introduced into commercial market in 1946 and remains till date the most used process for production of titanium in the world. However, as compared to other metals like iron, which are produced in a continuous manner, Kroll process produces the metal in batches of 10 tons maximum, with each batch taking several days. Titanium is reduced from rutile (TiO₂) to titanium metal in following two steps:

\[
\text{TiO}_2 + 2\text{Cl}_2 + \text{C} \rightarrow \text{TiCl}_4 + \text{CO}_2 \quad \text{chlorination} \quad \text{(eq. 2.1)}
\]

\[
\text{TiCl}_4 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgCl}_2 \quad \text{reduction} \quad \text{(eq. 2.2)}
\]

After reduction, vacuum distillation process is employed to clean titanium from salts. Further processing is done to produce titanium sponge. This sponge is ultra-high pure. However, due to titanium’s strong affinity to oxygen, a thin, passive oxide layer is always formed on the surface in oxidizing environments. Presence of reducing environments like sulfuric acid can cause the oxide layer to dissolve. This impervious oxide layer, although only 5-15 nm thick, is responsible for titanium’s excellent corrosion resistance even in some harsh environments.

2.1.2 Mechanical properties

Among all the structural metals, titanium has the highest strength to weight ratio. In addition to that, titanium’s excellent corrosion resistance properties and high temperature behavior make it a structural metal very attractive as compared to cheaper alternatives like steel. Density of pure titanium is around 4.5 g/cm³, much less than iron’s 7.874 g/cm³. Its strength, however, in absolute terms is lower than steel. Commercially pure titanium can have a tensile strength of around 550 MPa, whereas high strength titanium alloys can reach tensile strengths of 1200 MPa.¹

Alloying of titanium is generally done in order to fine tune mechanical properties of titanium. Alloying elements can be divided into two groups: interstitial and substitutional elements. Interstitial alloying elements, like carbon, oxygen and nitrogen, generally have a strong influence in increasing the strength, but at the same time have a detrimental embrittlement behavior. The ductility of the alloys decreases rapidly even with small additions of these interstitial elements. It is, therefore, common practice to keep the concentrations of these elements below 0.2 wt. %. Substitutional alloying elements, on the other hand, are much more suitable for increasing strength without much
loss in ductility. Elements like iron, manganese, aluminium, tin, vanadium and, molybdenum strengthen the alloys by solid solution strengthening, in addition to other effects.

2.1.3 Crystal structure

α phase and β phase are two most important of the several different crystal structures of titanium. Under normal conditions, pure titanium exists as α phase at room temperature. The α phase is a hexagonal closed packed (HCP) structure, with the following lattice cell parameters at room temperature: \( a = 2.95 \, \text{Å}; \, c = 4.68 \, \text{Å}; \, c/a = 1.59 \). Pure titanium with α phase structure undergoes a phase transformation when heated to temperatures above 882 °C, the so called transus temperature (\( T_p \)). The phase formed is called β phase, with body centered cubic (BCC) structure. The lattice parameter of β phase at 900 °C is \( a = 3.29 \, \text{Å} \). The densities of two phases are 4.50 g/cm³ for α phase at room temperature and 4.35 g/cm³ for β phase at 900 °C. The difference in density is essential for detection of the phase transformation by dilatometry.

Addition of either α or β stabilizers can be used to change \( T_p \) of the alloys. By adding the so called β stabilizers, like Fe, Mo, Cr and V, β phase can even be retained at room temperature, or a dual phase α + β structure can be obtained. The β stabilizers can be further subdivided into two categories: β-eutectoid elements and β-isomorphous elements. Examples of phase diagrams for both α and β stabilizers are given in Figure 2.1, Figure 2.2 and Figure 2.3. It can be seen from Figure 2.1 that small variations in oxygen content can change the transformation temperature of titanium considerably. It is, thus, very important to know the exact oxygen content of an alloy in order to calculated the transformation temperatures of a titanium alloy.

The β to α transformation can take place in two different ways. For very rapid cooling, a martensitic reaction can occur, resulting in martensite having orthorhombic (\( \alpha' \)) and/or HCP (\( \alpha'' \)) structure, dependent mostly on alloy composition. For lower cooling rates, again, two types of α can be formed. At higher temperatures, primary α is formed by nucleation and diffusional growth mechanism, whereas at lower temperatures, so called bainitic α (or black plates) is formed by displacive mechanism.³

![Figure 2.1: Part of phase diagram for Ti-O system showing that O is an α stabilizer.](image-url)
2.1.4 Classification of \( \beta \) alloys

Commercial titanium alloys are classified conventionally in three different categories as \( \alpha \), \( \alpha + \beta \) and \( \beta \) alloys according to their equilibrium constitution, which varies with the types and concentrations of alloying elements. The \( \beta \) alloys are further subdivided as \( \beta \) stable or \( \beta \) metastable alloys. This is shown in a schematic pseudobinary \( \beta \)-isomorphous phase diagram in Figure 2.4.

Figure 2.2: Part of phase diagram for Ti-Fe system showing that Fe is a \( \beta \) stabilizing element of \( \beta \)-eutectoid type.

Figure 2.3: Part of phase diagram for Ti-Mo system showing that Mo is a \( \beta \) stabilizing element of \( \beta \)-isomorphous type.
2.1.5 Applications
Titanium is not a very widely used structural metal, mainly due to its high cost. Still, titanium has carved out a niche for itself in fields like medical implants, due to its excellent bio-compatibility. Also, aerospace, storage and transport of hazardous materials are other fields of applications for titanium. Nowadays, with technology becoming more advanced, titanium is also being used in sports materials like golf clubs. However, application in automotive industry is rather limited, except for luxury vehicles.

2.2 Phases observed in titanium

2.2.1 Introduction
As described in § 2.1.3, depending on the thermal treatment and composition of the alloy, two different types of α products can form. In addition to athermal martensite forming for very high cooling rates, there is also another phase, called the ω phase, which is formed in some titanium alloys when β phase is quenched to room temperature. The following text in this section will give brief overviews for each of these phases.

2.2.2 Martensite
The martensitic transformation in titanium involves a cooperative movement of atoms, resulting in a microscopically homogeneous transformation of the BCC into HCP crystal lattice. Quenching of β phase (bcc) of pure Ti and dilute Ti-alloys can result essentially into two different crystal structures of athermal martensites: hexagonal martensite, designated by α' and orthorhombic martensite which is designated α''. The most prevalent type is α', which can occur in two limiting morphologies: massive or lath martensite (highly pure and very dilute alloys) and "acicular" martensite in alloys with slightly higher solute contents. Orthorhombic α'' seems to occur mainly in Ti-alloys with β stabilizers of transition metals Mo, Nb, Ta, W, Re and in Ti-alloys with Al + V. Lattice parameters of
α'' are strongly dependent on solute content, and the α'' crystal structure is sometimes conveniently viewed as distorted hexagonal structure. Especially for the case of Ti-Mo alloys, α' is observed for \( X_{\text{Mo}} < 4 \) wt%, which changes to α'' as Mo content is increased until about 10 wt%, above which the β structure is retained.

### 2.2.3 ω phase

All the Ti alloys in which β phase can be retained in a metastable state to room temperature by quenching form the ω phase having distorted (or undistorted) hexagonal or trigonal structure. A modified phase diagram including the ω phase formation temperatures is shown in Figure 2.5.

Figure 2.5: Schematic phase diagram of a β-isomorphous Ti alloy, showing ω phase formation regions.

The metastable ω phase can appear in the alloy systems under following conditions:

1. Over a limited range of solute content close to the lower limit for the retention of β phase, ω phase forms as a result of quenching from BCC phase. This is called athermal ω. In some alloys like Ti-Nb, however, ω formation is suppressed in as quenched samples because of the competing orthorhombic martensitic α'' transformation.

2. At high solute contents, the ω phase forms close to the so called ω start temperatures, \( T_{\omega} \). This is designated as isothermal ω because of the thermal activation required for transformation. During the course of ageing a metastable equilibrium (ω + β) state relative to (α + β) state is achieved. Also, ω formation during ageing is accompanied by a shift of lattice parameter of the β phase, indicating an enrichment of the β phase in the alloying elements.

In some alloys, deformation at room temperature is also shown to bring about transformation to ω phase under certain circumstances. Generally, it is not possible to detect the ω phase particles formed just after quenching because of the very low fraction and the very small size, a few Angstroms. Thus, detection of ω phase requires ageing, during which the ω particles increase in size and also an increase in hardness is observed.
2.2.4 Bainite or secondary α
Isothermal holding or continuous cooling of α + β titanium alloys can produce two distinctly different phases. The α phase formed at lower temperatures (away from $T_p$) is denoted as secondary α or bainite. It is characterized by relatively perfect thin plates (as compared to primary α) which nucleate both at the $β/β$ grain boundaries and intragranularly. Similar to primary α, bainitic α plates have Burgers’ orientation relationship with parent $β$ matrix (see § 2.2.5.4). There are, however, quite a few differences between the two types. Secondary α plates have smaller thickness to length ratio as compared to primary α. Also, etching characteristics of the two types are different. While primary α appears white after etching, secondary α plates appear dark, and hence are often called ‘black plates.’ Recently, the formation mechanism of bainite in titanium was reported to be quite different from primary α, which forms via a diffusional mechanism. Other differences in kinetics and surface relief were also observed. It was observed that the plates form without partitioning and then diffusion of solute elements takes place during further annealing. The interfacial structure of these plates consists of a ledged structure, having both structural and misfit ledges. For a detailed description of bainite, the reader is suggested to read M. Sc. thesis of Arjen Kamp.

2.2.5 Primary α

2.2.5.1 Introduction
At higher temperatures close to the $β$ transus temperature, $T_p$, a phase with plate like morphology is formed, called primary α. These α plates are generally irregularly shaped plates, which nucleate predominantly at the prior $β$ grain boundaries. The characteristics of primary α have been studied in quite detail by a few investigators. Although it is generally accepted that there are two main types of primary α (grain boundary α, which is formed along the $β/β$ grain boundaries and, Widmanstätten α, which is plate shaped and grows inside the $β$ grains) some authors also divide Widmanstätten α into two more sub-categories: Widmanstätten grain boundary and Widmanstätten intragranular. The various aspects of primary α will be discussed next.

2.2.5.2 Morphology
The first detailed study on formation of α in titanium alloys was conducted in 1957 by Aaronson et al. They studied both primary α and secondary α in a Ti-Cr alloy. It was reported that so called grain boundary allotriomorphs are the first morphology to precipitate at $β/β$ grain boundaries in the temperature range for formation of primary α. These are not the predominant morphology at late reaction times at any temperature, but are the initially dominant morphology. It was also reported that thickening of allotriomorphs is not halted even when the proportion of α in the microstructure becomes constant. The Widmanstätten sideplates grow from the grain boundary allotriomorphs and are formed in groups which are parallel to a common habit plane in the $β$ grain into which they develop. Moreover, if the $β/β$ grain boundary is curved, then formation of the sideplates can even be prevented. Aaronson et al. found that the sideplates were often made up of short segments, which they called beads. These segments were explained to be separate α grains nucleated on a growing $α/β$ interface by sympathetic nucleation (discussed in § 2.3.2). They also reported that as the reaction time increases, the average spacing between the sideplates increases, the perfection of shape of sideplates increases, the connections between sideplates and allotriomorphs are severed and the sideplates tend to break up into smaller segments. Formation of intragranular Widmanstätten plates takes place at longer reaction times. These plates appear as isolated single plates or grouped together in sheaves.
The Widmanstätten intragranular ($\alpha_{wi}$) morphology is observed to form at lower reaction temperatures than the grain boundary $\alpha$ ($\alpha_{gbb}$) and the Widmanstätten grain boundary $\alpha$ ($\alpha_{wgb}$). However, the $\alpha_{wi}$ plates do not appear as gathered in colonies, like $\alpha_{wgb}$, but form basketweave patterns.

Based on the heat treatments carried out in this project, the morphology of primary $\alpha$ is divided into two main categories- grain boundary $\alpha$ and Widmanstätten $\alpha$. Examples of different morphologies of the two types are given in Figure 2.6 and Figure 2.7.

![Figure 2.6: Different morphologies of grain boundary $\alpha$. (A) Full $\beta/\beta$ grain boundary coverage. (B) Zigzag morphology. (C) High nucleation density at the $\beta/\beta$ grain boundary.](image)
2.2.5.3 Nucleation and growth kinetics

The nucleation and growth kinetics of primary α plates have been studied by various authors and a few attempts on modeling have also been carried out. The first attempt by Menon and Aaronson was based on calculating the fraction transformed from examination of optical micrographs of isothermally annealed samples. They plotted number of γ_{GB} grains formed as a function of time at various temperatures and also studied the thickening and lengthening behavior of the allotriomorphs. The results were modeled using the pillbox model for nucleation rate and diffusional model by Cahn for growth kinetics. It was proposed that the transformation of γ_{GBA} is purely diffusion controlled.

Afterwards, Semiatin et al., Da Costa Teixeira et al., Malinov and Sha, Appolaire et al., among others, used diffusional models like JMAK and ‘constant-radius’ approximation to describe the kinetics of primary α in general. Although the results were satisfactorily good, some of these studies used approximations which were not correct. For example, in Ref. [10], hard impingement was incorporated as one of the assumptions in order to be able to use the extended volume condition in JMAK law. However, the diffusional mode of transformation in this partitioning transformation means that soft impingement is the underlying phenomenon, at least for low volume fractions of α. Some attempts on using mixed mode model and phase field model have also been made. Still, the understanding of the nucleation and growth kinetics for primary α is not complete till date.

2.2.5.4 Orientation relationship

For the case of BCC-HCP transformations, there are a few orientation relationships which have been proposed in literature. These orientation relationships are given in Table 2.1.
Table 2.1: Possible orientation relationships in a BCC-HCP transformation.

<table>
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<tr>
<th>Orientation Relationship</th>
<th>Parallel planes and directions</th>
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<tr>
<td>Burgers</td>
<td>$(0001)<em>{hcp} \parallel (011)</em>{bcc}, [1\bar{1}20] \parallel [1\bar{1}1]$</td>
</tr>
<tr>
<td>Potter</td>
<td>$(0001)<em>{hcp} 2° from (011)</em>{bcc}, (01\bar{1}1)<em>{hcp} \parallel (1\bar{1}0)</em>{bcc}, [1\bar{1}20]<em>{hcp} \parallel [1\bar{1}1]</em>{bcc}$</td>
</tr>
<tr>
<td>Pitsch-Schrader</td>
<td>$(0001)<em>{hcp} \parallel (011)</em>{bcc}, [1\bar{1}20]<em>{hcp} \parallel [100]</em>{bcc}$</td>
</tr>
<tr>
<td>Rong-Dunlop</td>
<td>$(0001)<em>{hcp} \parallel (021)</em>{bcc}, (1\bar{1}00)<em>{hcp} \parallel (0\bar{1}2)</em>{bcc}, [1\bar{1}20]<em>{hcp} \parallel [100]</em>{bcc}$</td>
</tr>
</tbody>
</table>

Numerous studies\textsuperscript{15,16,17,18,19} have confirmed that for titanium alloys Burgers’ orientation relationship\textsuperscript{20} is obeyed best. In total, there can be 12 variants of the Burgers’ orientation relationship (OR). One of the variants is shown in Figure 2.8. It is generally accepted that there might exist a misfit of a few degrees from the orientation relationship, which is attributed to the high reaction temperatures.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2_8.png}
\caption{One of the variants of the Burgers’ OR showing \((0001)_{\alpha}\) superimposed on \((110)_{\beta}\) (hexagon is \((0001)_{\alpha}\) and rectangle is \((110)_{\beta}\).}
\end{figure}

2.2.5.5 Growth direction of plates and interfacial structure

The TEM studies\textsuperscript{15,21,22} carried out on Ti alloys to study the structure \(\alpha/\beta\) interface and growth directions of \(\alpha\) were comprehensively analyzed by Furuhara et al.,\textsuperscript{23} in which they compiled the previous studies and tried to formulate a full explanation. It was found that the \(\alpha/\beta\) interface consists of a ledged structure, having both structural and misfit ledges. A few terms need to be defined first. The structural ledges reduce the interfacial energy due to higher coherency whereas misfit ledges compensate for misfit of the two lattices by creating extra half planes; these are also called misfit dislocations. When one phase transforms into the other, a significant transformation strain is generated. The lattice invariant line is the direction along which there is no transformation strain, or in other terms, atomic positions along that direction remain unchanged during the phase transformation. The broad face of a plate is the interface having lowest interfacial energy, formed
because the grain grows in other directions faster than perpendicular to the broad face. This is due to the lower mobility of lower energy interface.

It was observed that the macroscopic broad face of $\alpha$ plates lies along the lattice invariant line due to least strain conditions. However, this broad face is not coherent. In order to increase the coherency and, in turn, decrease the interfacial energy, structural ledges are formed on the interface. The spacing of the structural ledges is governed by the angle between the macroscopic broad face and the structural ledge formed. In case of $\alpha$ plates in titanium, it was found that the broad face is approximately $(1\overline{1}1)_\beta$ plane and the lattice invariant line is $[5\overline{3}3]_\beta \parallel [5\overline{13} \overline{1}8 0]_\alpha$. The ledge plane is $(1\overline{1}2)_\beta \parallel (1\overline{0}0)_\alpha$ and is at an angle of $14.4^\circ$ with the macroscopic broad face. A schematic of this morphology is shown in Figure 2.9.

However, there are a few discrepancies in this explanation. Firstly, this kind of interface is not observed for longer reaction times in some cases. The explanation from Furuhara et al. was that when annealing time is increased, the low energy interface is replaced by some interface of even lower energy. Secondly, they did not explain the growth kinetics of the edge and side facet (Figure 2.9 B). The only case that they studied was when they had to explain the thickening behavior of the plates, which they did by explaining that growth of ledges is the underlying mechanism.
2.2.5.6 Phase composition

Only a few studies have been done to investigate the composition of primary $\alpha$ plates in titanium. Enomoto and Fujita$^{24}$ investigated the composition of $\alpha$ plates formed in four different titanium alloys. The authors described in their introduction the differences between primary $\alpha$ and secondary $\alpha$ plates that can be found in titanium. However, it is unclear which type of plates they have investigated. For the Ti-Fe alloy, they gave a TEM micrograph and the annealing characteristics and, for the Ti-V alloy, they gave only the annealing characteristics without further explanation.

The distribution of alloying elements was measured in a Scanning Transmission Electron Microscope (STEM) equipped with an Energy Dispersive X-Ray (EDX) analyzer.$^{24}$ All the alloys were heat treated in a way so as to study the very start of the transformation. In the Ti-Fe alloy, the Fe concentration was measured along two different paths. The Fe concentrations were found to be uniform within the primary $\alpha$ plates, but two points along the measured path were supersaturated with Fe. One point was actually on the plate tip and the other was approximately 0.3 $\mu$m behind the plate tip. However, the effect was attributed to $\beta$ matrix contribution to X-rays. In the Ti-V alloy, it was seen that the V concentration inside the $\alpha$ plate was uniform and there was a solute buildup at the $\beta$ side of the $\alpha/\beta$ interface, with the concentration decaying to bulk concentration in the interior of $\beta$ grain. When the concentration of alloying elements was studied for different isothermal holding times, it was observed that the concentration of Fe and V in $\alpha$ remained constant with time, whereas the concentration in $\beta$ increased with time due to an increase in $\alpha$ phase fraction. The authors concluded that the growth of $\alpha$ plates was diffusion controlled with two different arguments. First, they observed there was no clear evidence of partial partitioning of the solute, that is, no spot in the $\alpha$ plates had composition half way towards the equilibrium. Secondly, they found that the composition of $\alpha$ plates corresponded to almost the equilibrium values, even at very early reaction times. Also, the plates had formed well above the $T_0$ temperature (temperature at which free energies of $\alpha$ and $\beta$ phase are equal) and thus the plates had formed by a partitioning mechanism.

Ohmori et al.$^{25}$ studied the V concentration of $\alpha$ plates in a Ti-6Al-4V alloy for different isothermal annealing times using Wavelength Dispersive Spectrometry (WDS). They found that at the same isothermal annealing temperature, no solute partitioning was observed for very small reaction times, whereas V partitioned to a considerable extent if the reaction time was increased. Although this suggests that the formation of these $\alpha$ plates does not proceed via a conventional diffusional mechanism under ortho-equilibrium conditions, the authors did not emphasize much on this point.

2.3 Interface destabilization and sympathetic nucleation

2.3.1 Interface destabilization

Interface destabilization can be defined as morphological instability of planar boundaries growing during a solid/solid or solid/liquid phase transformation. For the case of solidification, this phenomenon is also called constitutional supercooling. It occurs when, due to partitioning of solute atoms, the leading front in a perturbation formed on a planar interface has higher undercooling than the trailing front. The leading front would thus have higher velocity than the trailing front, causing the interface to destabilize from planar shape. An example of such effect is shown in Figure 2.10, and shape of a destabilized interface is shown in Figure 2.11.
Figure 2.10: Example of constitutional supercooling during solidification.

Figure 2.11: Typical shape of a destabilized interface during initial stages of growth.

In analogy, the same principle applied to solid/solid transformation for systems having considerable partitioning, was proposed by Townsend and Kirkaldy,\textsuperscript{26} to explain the formation of Widmanstätten ferrite in case of steels. For the case of partitioning during a transformation, and diffusion controlled growth, they proposed that any perturbation formed on the growing planar interface would grow out ahead of the planar interface due to the higher gradient in front of it. This is shown schematically in Figure 2.12, for the case in which solute diffuses in a direction opposite to the interface growth direction. The leading front has a higher concentration gradient, and thus, can grow with a higher velocity.

Figure 2.12: Interface instability in solid/solid transformations.
This concept, however, lost ground after Aaronson proposed sympathetic nucleation for the same reaction, which is described in \S\ 2.3.2. Recent studies on Al-Cu systems\textsuperscript{27} and Al-Cu bimetal thin films\textsuperscript{28} have shown some observational proof towards validating this phenomenon in solid/solid transformations. There was also a study on Ti alloys,\textsuperscript{29} in which, using TEM analysis, V (\(\beta\) stabilizer) concentration build-up at the trailing region was observed, giving indirect proof of decrease in interface velocity in the trailing region.

The following mechanisms of interface stabilization in case of solid/solid transformations have been proposed:\textsuperscript{30}

(a) Overlapping diffusion fields and size effects;
(b) Interface controlled growth assisted with the ledge mechanism;
(c) Stabilization by transformation stresses; and
(d) Anisotropic interfacial energy.

Out of these four possible, the first contribution to stabilization is particularly important. Even if the other three mechanisms were not contributing to interface stabilization, a planar interface will tend to be stable if the gradient is very small at the interface because of overlapping diffusion fields and/or if the size of the precipitate is very small (the possible wavelength of the instability is very small). The second mechanism of interface stabilization is very difficult to study because there are very few experimental results in literature that suggest a detailed mechanism by which morphological instabilities can occur concurrently with the ledge mechanism of growth. This is also because the studies on atomic level dynamics are mainly focused on dilute solid solutions, where interface instabilities are unlikely to occur due to solute depletion effects. However, if there are two solute elements which diffuse in opposite directions, like for the alloy studied in this project (Al and Mo/Fe), the second mechanism gets reduced in magnitude and can be neglected. The third and fourth mechanisms are very difficult to study experimentally and there have not been any validations of these contributions, although, qualitative explanations are abound.\textsuperscript{30}

2.3.2 Sympathetic nucleation

Sympathetic nucleation, as defined by Aaronson,\textsuperscript{31,32,33} is a process in which nucleation of a precipitate crystal occurs at the interphase boundary of another crystal of the same phase with the matrix. A schematic of sympathetic nucleation is given in Figure 2.13. This was used to explain the Widmanstätten type morphology observed in steel. The phenomenon, first identified by Aaronson and Wells\textsuperscript{31} for steel in 1956, was explained as destruction of \(\gamma/\alpha\) boundaries by sympathetic nucleation of \(\alpha\) nuclei at them, which assists the overall nucleation process. They were, however, not able to explain how sufficient driving force could be acquired for such a nucleation. In 1965, Shewmon\textsuperscript{34} overcame this problem by explaining that the immobile terraces of growth ledges at partially or fully coherent interphase boundaries would provide a smaller contribution to interfacial energy but a much larger supersaturation through which to drive the nucleation process. He also showed that a slow interfacial reaction, i.e. low interface mobility, would stabilize the growing interface, thus increasing the tendency for sympathetic nucleation. However, he did put forward the idea that a growing interface would be stable, until a maximum value of \(\sqrt{Dt}\) of the wavelength of the perturbation was reached, whereupon the interface could destabilize, given that the reaction was diffusion controlled. Also, if the interfacial reaction is rate determining, the tendency to instability is greatly reduced from that in the case of diffusion controlled growth.
Later, Menon and Aaronson\textsuperscript{32} observed, for a Ti-Cr alloy, the presence of low energy $\alpha/\alpha$ grain boundaries. These low energy grain boundaries were either of small angle type or near-CSL boundaries. They also claimed, analytically, that it is impossible to have branching in different directions while maintaining an equivalent pair of conjugate habit planes, thus proposing that sympathetic nucleation was the only possibility to explain the observed morphologies. Also, they showed that sympathetic nucleation was highly favorable because it replaced a high energy precipitate/matrix boundary with a low energy precipitate/precipitate boundary. Spanos et al.\textsuperscript{35} have recently shown using TEM that the Widmanstätten sideplates in steel consist of ferrite grains having small angle grain boundaries between them.

Supersaturation required for sympathetic nucleation is available at the terraces of growth ledges on partially coherent boundaries. The calculations by Aaronson et al.\textsuperscript{33} based on finite difference method indicated that this supersaturation is largest at the riser bounding a given terrace during earlier reaction times, when solute diffusion is restricted mainly to the region directly in front and back of the riser. When a larger region is available in which to disperse or ingest solute, however, supersaturation at terraces is greater at later growth times (proposed in Ref. [33]).

The three configurations of sympathetic nucleation are shown in Figure 2.14. From the perspective of the current alloy, only edge to edge nucleation is of importance and will be the only one explained. Aaronson et al.\textsuperscript{33} have reported this kind of behavior to be present quite frequently in steel and Ti-X alloys (X is the alloying element). Their explanation was that if, during the lengthening of a plate (or lath or needle), the supply of growth ledges at the leading edge temporarily “dries up”, edge-to-edge sympathetic nucleation would take place. Sympathetic nucleation then would have much enhanced opportunity to take place at a stationary partially coherent facet at which supersaturation is (temporarily) not being diminished by the solute build-up or depletion at an advancing growth ledge. Also, edge-to-edge configuration requires higher energy for nucleation, thus the requirement for large supersaturation and high $\alpha/\beta$ interfacial energy at the leading edge. This explanation, however, was not based on an experimental fact, but was rather a speculative interpretation of the observations. Aaronson et al.\textsuperscript{32} also built up on Shewmon’s explanation by proposing that the supersaturation required for sympathetic nucleation is available at the terraces of growth ledges on partially coherent boundaries between two crystals differing significantly in composition.
1. **Face-to-face SN**
   (sheaves)

2. **Edge-to-face SN**

3. **Edge-to-edge SN**

Figure 2.14: Configurations of sympathetic nucleation.

Sympathetic nucleation is frequently observed in eutectoid type systems like Cu base, Fe-Fe₃C-base, Ti-Cr alloys. However, aging type systems like Al base alloys do not exhibit sympathetic nucleation. This kind of behavior has been tried to be explained as follows: In case of eutectoid systems, supersaturation ratio of the order of 10 or more is usually observed, whereas in case of aging systems, it can be even 1.1 or less. This low amount of supersaturation in case of aging systems cannot provide enough driving force for nucleation.
Chapter 3 Experimental techniques

3.1 Background and theory of experimental techniques

3.1.1 Serial sectioning and 3-D analysis of titanium

Microstructural features used for understanding of and developing models for phase transformations in metals are usually obtained from the surface of polished specimens. However, in order to come to a description of the actual microstructure, this approach requires stereological analyses to convert two-dimensional features into three dimensions, which can lead to serious errors. Serial sectioning can be defined as the process of successive removal of sections of a certain thickness of a material. The history of 3-D analysis in metallography spans at least from 1918 with Forsman’s serial sectioning effort to understand the 3-D structure of pearlite. He constructed solid models of cementite lamellae by projecting the images of each section onto cardboard layers of appropriate thickness. However, it took another 44 years till Hillert and Lange were able to successfully show the true 3-D structure of an entire pearlite colony. Making a motion picture, they were the first ones to demonstrate experimental evidence of interconnectivity of ferrite in pearlite.

The past four decades have witnessed significant improvements in 3-D analysis. Although currently newer techniques for three-dimensional characterization like dual beam focused ion beam scanning electron microscopy (FIB SEM) and 3-D XRD have become available, serial sectioning still remains a very widely employed technique. This is mainly because both FIB-SEM and 3-D XRD techniques suffer from various disadvantages. The FIB-SEM technique is characterized by a considerable resolution, but suffers from the drawback that the maximum observed volume is still quite small. 3D-XRD reaches a similar resolution as serial sectioning, but is, apart from being very time consuming, not readily accessible.

The most notable studies in serial sectioning started with the advent of sophisticated computer programs in the early 1990s. The ease of reconstruction of the structures in three dimensions made it possible for detailed 3-D analysis of various alloy systems. Most serial sectioning studies have been performed on steel microstructures, such as pro-eutectoid ferrite, pearlite, Widmanstätten ferrite and cementite. In addition, some microstructures in Ni-alloys and Al-alloys have been investigated.

For the case of titanium alloys, the first attempt was made by Hull et al. to characterize the prior \( \beta \) grain volume distribution. They used a Ti-Al-Sn-Zr-Nb-Mo alloy and carried out serial sectioning with a section thickness of 10 \( \mu \)m. By using the commercial software CATIA, they were able to reconstruct the \( \beta \) grains shape for the alloy with a reasonable accuracy. Guo and Enomoto carried out surface relief analysis on \( \alpha \) plates formed on a polished surface using Atomic Force Microscopy (AFM). They also used serial sectioning to investigate nucleation sites for intragranular plates and found that \( \beta/\beta \) grain boundaries were the primary sites for nucleation. Tiley et al. and Searles et al. developed stereological methods for analysis of microstructures in titanium alloys and validated them by carrying out serial sectioning on an \( \alpha + \beta \) alloy with predominantly \( \alpha \) microstructure. Furthermore, Vanderesse et al. carried out 3-D microtomographic study of an \( \alpha + \beta \) titanium alloy to reconstruct a Widmanstätten colony.

Quite recently, Lewis et al. and Rowenhorst et al. combined EBSD and serial sectioning for two different types of steel microstructures. It was shown that important information like nucleation
sites, growth mechanisms and variant selection require both orientation information and three-dimensional features. This approach will also be applied in the present work.

3.1.2 EBSD

3.1.2.1 Principles and setup

Electron back-scattered diffraction, EBSD, is a technique based on the acquisition of precise crystallographic orientations from the surface of bulk samples in the scanning electron microscope (SEM). EBSD is carried out on a specimen tilted around 70° from the horizontal plane which is stroked by a stationary electron beam. The diffracted electrons are captured by a phosphor screen where an electron backscatter pattern, EBSP, is formed. Crystallographic orientation information is quantitatively obtained from this EBSP. The mechanism by which the diffraction patterns are formed is complex and a brief description is given below.

The electron beam produced by the SEM is directed on a small area of the tilted sample where primary electrons are diffusely scattered in all directions, and consequently part of them strike on a given set of lattice planes \((hkl)\) at the Bragg angle, \(\theta\), satisfying Bragg’s equation, given by

\[
2d_{(hkl)} \sin \theta = n \lambda
\]  

(eq. 3.1)

where \(d_{(hkl)}\) is the interplanar spacing between the diffracting planes, \(n\) is the order of reflection and \(\lambda\) is the electron beam wavelength, which is dependent on the electron beam energy. The trajectories of the scatter electrons, hereinafter referred as backscatter electrons, produce two cones on either side of the diffracting set of planes with an apex half-angle of \((90°-\theta)\) around the plane normal <hkl>. These are known as Kossel cones. When the backscattered electrons are recorded on a phosphor-coated glass screen, the interception of a pair of Kossel cones with the screen is seen as a pair of hyperbolas, which approximate as straight lines because \(\theta\) is relatively small (~1.4°). The set of straight lines or bands formed on the phosphor screen are referred as electron back-scattered patterns, EBSP, also known as Kikuchi line patterns due to their resemblance to the diffraction patterns that form during transmission electron microscopy (TEM). An example of a Kikuchi pattern is shown in Figure 3.1. The bands in the EBSP represent planes in the crystal where the widths of the bands are a function of the \(d\)-spacing of the corresponding crystallographic planes. The angles between bands in the patterns are directly related to the interplanar angles in the crystal lattice. The full process is shown schematically in Figure 3.2 with silicon crystal as an example. After the planes related to pairs of bands have been identified, the orientation of the crystal can be obtained with an angular precision of approximately 1°, although it can be further improved by using FEG-SEM equipment. The identification is usually done by comparing the recorded data with stored patterns in a database.
The basic EBSD installation (Figure 3.3) consists of a video camera coupled to a phosphor screen, a camera control and a diffraction processing unit, all connected to a computer. The computer is installed with a data processing and analysis software. In most cases, automatic data processing is a proper and reliable method of determining the structure and the orientation. However, during EBSD patterning, some practical difficulties may arise which need to be dealt with. For some orientations, Kikuchi patterns are difficult to distinguish from each other within the resolution of the imaging system. This is called 'Pseudosymmetry.' This can either be resolved by using a cleanup tool in the analysis software, or by adjusting the number of Kikuchi bands used for orientation determination.
3.1.2.2 Pole figures and inverse pole figures

One popular method adopted to visualize crystal orientations is related to stereographic projections, i.e. representation of three-dimensional angular relationships in two dimensions by the use of the concept of unit spherical projection. This concept allows for two different methods to represent crystal orientations: the pole figure and the inverse pole figure. In the case of pole figures, the crystal structure is placed on the centre of the unit reference sphere, linked to the sample reference system (often ND, TD, RD), and specific directions or plane normals are extended until they intersect the reference sphere. This pole is later projected on the equatorial plane in such a way as is illustrated in Figure 3.4 and the intersection point is referred as pole of the respective crystal lattice planes. Finally, the equatorial plane and the poles are represented on two dimensional plots. If the coordinate systems are interchanged, that is, if crystal reference is linked to the spherical projection and the sample reference system is located in the centre of the spherical projection, then this representation is referred to as inverse pole figure.

Figure 3.4: Construction of a <100> pole figure on the unit reference sphere.
The pole figures allow a physical visualization about the orientation of the crystal cell in the reference frame. However, this information can become ambiguous if there is more than one orientation because each orientation is determined by several poles which cannot be associated to a specific orientation in a unique way. Then it is needed to construct at least three poles to satisfactorily determine the crystal orientation.

### 3.1.3 FIB 3D-EBSD

This technique involves removal of sections from sample surface, like in serial sectioning, by ion milling using a Focused Ion Beam (FIB). Using this technique, it is possible to ion mill a series of slices (as thin as 50 nm), map these slices consecutively by EBSD and then generate 3-D crystallographic maps using computer procedures. In the setup used in this project, the first step, that is ion milling, is achieved by targeting an ion beam onto a predetermined area of the sample, in such a way that the ion beam just scrapes the surface. This means that ion milling is best done on edge regions. The reason for this requirement is that if the ion beam is perpendicular to the surface where sectioning is to be done, the impact of ions on the surface would lead to a lot of deformation and ion embedment on the surface. The ions generally used for milling are Ga⁺ ions. Energy of the ion beam also decides damage to the sample surface. The time required for acquisition of 3-D microtexture depends on several factors, such as the material, the capabilities of the equipment and the resolution of data; although the time is mainly distributed between EBSD acquisition time (~45%), FIB milling time (~35%) and positioning of the sample between both stages. A schematic of the process is given in Figure 3.5. This process has the advantage that very high resolution, both horizontal and lateral, can be achieved along with full orientation data. However, the same advantage also serves as a disadvantage because, as compared to other methods like conventional serial sectioning, the maximum volume that can be studied is quite small due to time limitations.

![Figure 3.5: Schematic representation of sample position during the two consecutive steps of measurement.](image) (A) Sample in milling position. (B) Sample in EBSD position. RD, ND and TD are the axes of the sample coordinate system. 1- Sample; 2- EBSD detector; 3- Electron Gun.
3.1.4 WDS
Wavelength dispersive spectrometry, or WDS, is a powerful tool for accurate microanalysis of chemical constituents of a solid. It is based on the principle of detection and quantification of characteristic X-rays.

When an electron beam is incident on a sample surface, incident electrons and the atoms of the solid interact in different ways. If the incident beam energy exceeds the energy required to eject an electron from an atom in the specimen, then there exists a finite probability of such an ionization event occurring. Ionization of the atom occurs by an inelastic scattering event which raises the energy of the atom above the ground state by an amount equal to the ionization energy. The energy of the atom can then decay by an electron transition into the now vacant state. All such transitions are accompanied by the emission of a photon, and if the energy of the excited state corresponds to the ejection of an electron from one of the inner shells of the atom, then this photon will have energy in the X-ray region of the spectrum. In general, decay of an atom from the excited state takes place in more than one stage, with the emission of several photons of different wavelengths, each corresponding to a transition of the excited atom back towards the ground state. A schematic of this process is given in Figure 3.6.

![Figure 3.6: Schematic of X-ray emission process. State means energy of the atom having a vacant electron site in the corresponding shell.](image)

The wavelengths of the characteristic lines which are emitted constitute a fingerprint of the elements present in the solid and provide a powerful method of identifying the chemical constituents and their distribution. However, it must be mentioned that rather than a single line, groups of lines are emitted, and there may be overlap between the lines emitted by one chemical constituent and those emitted by a second component. Also, a fraction of X-rays generated are absorbed by the sample itself. The X-ray signal emitted comes from a volume element defined by the envelope of electron energies which exceed the energy required to excite the characteristic radiation of interest. As the beam voltage is reduced, so this volume element shrinks, thus improving the potential spatial resolution, but at the same time reducing the emitted X-ray signal. A
compromise has to be made in order to ensure that the signal remains statistically significant but still spatially localized. One way to get around this problem is to increase the time for collection of the signal.

Detection of the emitted signal presents two main problems. First, the detector only covers a limited solid angle at the sample, and only those X-rays that reach the detector have any chance of detection. As the X-rays are emitted in all directions, significant fraction is lost. Secondly, the detector itself has a limited detection efficiency which also depends on the wavelength of the incident photon. Similarly, perfect discrimination (energy resolution) would require that the wavelength of each photon counted should be accurately known and distinguishable from any activation events taking place at the detector which are associated with photons of different wavelength. This is also impossible because of overlapping background white radiation (which implies an uncertainty in the source of the photon).

The system of WDS (Figure 3.7) employs a series of bent single crystals to cover the range of wavelengths which are of interest, and the wavelength within each range is scanned, adjusting the angle $\theta_0$ by rotating and moving the crystal and moving the detector. The single crystal is used for diffracting the X-rays according to Bragg's equation (eq. 3.1). This setup allows for detection of intensity of photons of single wavelength with high accuracy and then change to another wavelength. Thus, there is also the problem that each wavelength has to be scanned separately and the process becomes time consuming, unlike energy dispersive spectroscopy (EDS), where all the wavelengths are detected simultaneously. However, as compared to EDS, WDS has much better energy resolution and is especially suited for light elements like C or O. Although Auger Electron Spectroscopy (AES) is even better for elements with low atomic number, it suffers from the drawback that the depth of sample from which signal is acquired is of the order of a few Angstroms and for the case of titanium, it will scan only the oxide layer.

![Figure 3.7: Setup for WDS.](image-url)
Elemental detection in titanium poses two main problems. Firstly, an oxide layer (TiO₂) is always present on the metal surface. When calculating the amount of solute elements, proper care needs to be taken to adjust for the oxide layer. A schematic of this is shown in Figure 3.8. A significant amount of X-rays generated come from the oxide layer which is pure TiO₂. Thus, if the signal from oxide layer is not properly accounted for, the quantification will give results not representative of the actual condition.

Secondly, and this one is general to any types of alloys, the depth under the surface of sample from which the signal comes depends on the energy of the X-rays, which, in turn, depends on the type of element. If, for example, Ti and Mo are both present in the sample (50 – 50 at%), the X-rays corresponding to Mo will come from different depth than the X-rays corresponding to Ti, and will have different intensities, although the number of atoms of each type is the same. Thus, it is very important to use an accurate correction method that takes all these effects into account.

### 3.2 Experimental

#### 3.2.1 Composition and heat treatments

The commercial name of the titanium alloy investigated in this work is Titanium Low Cost Beta alloy (Ti-LCB). The chemical composition, as measured by X-ray fluorescence spectroscopy (XRF) is given in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Fe</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>6.7</td>
<td>4.3</td>
<td>1.5</td>
<td>balance</td>
</tr>
<tr>
<td>at. %</td>
<td>3.4</td>
<td>3.8</td>
<td>2.7</td>
<td>balance</td>
</tr>
</tbody>
</table>
The $\beta$-transus temperature ($T_p$) for this alloy, as calculated from experiments, is 800 °C. The phase diagrams for the alloy showing the equilibrium concentrations of different alloying elements at different temperatures, as calculated from Thermocalc, are given in Figure 3.9, Figure 3.10 and Figure 3.11. A schematic of the TTT curve for this alloy is given in Figure 3.12. The region for martensite formation is not understood right now and is not shown. The alloy was received in the form of a rod of diameter 15 mm and samples measuring 4.5 mm in diameter and 10 mm in length were cut out. The heat treatments were carried out in a Bähr 805 A/D dilatometer. A schematic illustration of the dilatometer is given in Figure 3.13. The length change is measured with a Linear Variable Displacement Transducer (LVDT). The $\beta$ to primary $\alpha$ transformation is accompanied by a small negative change in length $\Delta L$. However, between 730 °C - 800 °C, $\Delta L$ is too small for straightforward analysis. Thus, the dilatometer was used for its excellent vacuum and temperature control and not for length change analysis.

![Figure 3.9: Phase diagram of the alloy studied, with respect to molybdenum content.](image)

![Figure 3.10: Phase diagram of the alloy studied, with respect to iron content.](image)
Figure 3.11: Phase diagram of the alloy studied, with respect to aluminium content.

Figure 3.12: Schematic TTT curve for the alloy studied.
A thermocouple was spot welded in the middle of each sample for temperature control. Samples were held loosely between the two quartz rods and were heated to a temperature above $T_\beta$ at a pressure of less than $4 \times 10^{-5}$ mbar and held for a fixed amount of time in order to get a homogeneous structure consisting of only $\beta$ grains. This step is also called solutionizing. The samples were then cooled rapidly to the isothermal holding temperature in approximately 2 seconds to prevent any transformation during cooling. After isothermal annealing, the microstructures formed were frozen by cooling the samples to room temperature at a cooling rate of approximately 40 °C/s, which is fast enough to prevent any formation of secondary $\alpha$ phase. During cooling below a certain temperature ($\approx 400$ °C), formation of nano-sized athermal $\omega$ precipitates takes place inside the remaining $\beta$ grains, but they do not appear in the analysis of microstructures as they can only be resolved by employing high resolution microscopy. In some cases, however, martensitic plates were also observed, but they do not affect the analysis of $\alpha$ grains. Details of the heat treatments discussed in the thesis are given in Table 3.2. Rest of the heat treatments along with respective microstructures are given in Appendix A.

**Table 3.2: Overview of heat treatments.**

<table>
<thead>
<tr>
<th>Heat treatment #</th>
<th>Solutionizing temp. (°C)</th>
<th>Solutionizing time (min)</th>
<th>Isothermal annealing temperature (°C)</th>
<th>Isothermal annealing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>10</td>
<td>615</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>900</td>
<td>10</td>
<td>680</td>
<td>50</td>
</tr>
<tr>
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<td>10</td>
<td>700</td>
<td>30</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>900</td>
<td>10</td>
<td>735</td>
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<td>8</td>
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<td>12</td>
<td>900</td>
<td>2160</td>
<td>730</td>
<td>50</td>
</tr>
</tbody>
</table>
After heat treatment, each sample was cut into two halves in order to analyze the microstructure in bulk of the samples.

### 3.2.2 Sample preparation and optical microscopy

In order to prepare the samples for optical microscopy, a polishing procedure similar to the one recommended by Struers was employed. After embedding in a mounting resin or using a sample holder made of brass, all samples were plane ground according to the grinding matrix given in Table 3.3.

**Table 3.3: Grinding matrix.**

<table>
<thead>
<tr>
<th>Step #</th>
<th>Grit (abrasive type)</th>
<th>Disc revolution speed (rpm)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>220 (MD Piano)</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>220 (SiC paper)</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>500 (SiC paper)</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>800 (SiC paper)</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>1200 (SiC paper)</td>
<td>150</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>2400 (SiC paper)</td>
<td>150</td>
<td>360</td>
</tr>
<tr>
<td>7</td>
<td>4000 (SiC paper)</td>
<td>150</td>
<td>360</td>
</tr>
</tbody>
</table>

Grinding was followed by fine polishing using a 30% v/v solution of H$_2$O$_2$ and colloidal silica (OP-S) for 10 minutes. The addition of H$_2$O$_2$ to OP-S is very important because it reacts with the deformed layer on the surface, thus making it brittle and effecting its removal. This allows for a deformation-free surface finish of the samples. Special care has to be taken while polishing titanium because it is very ductile, thus diamond paste cannot be employed. Furthermore, the force on the samples was kept to a minimum of 10 N in order to avoid deformation of the softer $\beta$ phase. For EBSD, it is generally recommended to carry out electrolytic polishing after the aforementioned polishing steps, in order to ensure deformation-free sample surface. It was, however, found that electrolytic polishing carried out following the procedure described by Kamp etched the sample and then EBSD scans had the problem of shadowing. Also H$_2$O$_2$ addition makes it possible for the sample to be used for EBSD directly after fine polishing. For etching, Kroll etching solution (90 ml water, 3 ml HF and 7 ml HNO$_3$) was used. Samples to be further used for EBSD, WDS and FIB 3D-EBSD analysis were covered with a removable resin in order to protect the surface from accidental damage during storage and transportation. Optical micrographs were taken using an Olympus BX60M Optical Microscope.

### 3.2.3 Serial sectioning

Serial sectioning procedure needs accurate determination of section thickness, i.e. thickness of the layer removed after each sectioning step. In order to achieve this, the following procedure was employed. 17 different regions in different samples were chosen and Vickers' hardness indents were made using a Buehler Omnimet Microhardness tester for subsequent section alignment. An example of such a region is shown in Figure 3.14. Samples were fine polished using the OP-S and H$_2$O$_2$...
solution to remove a section. The thickness of section removed was calculated using reduction in size of the hardness indents. In order to determine the relationship between the polishing time and section thickness ($\Delta z$) and to examine the precision in $\Delta z$, dummy samples were polished for varying amounts of time. A variance of $\pm 0.05 \, \mu m$ was observed in $\Delta z$. It was found that relationship between polishing time and $\Delta z$ is not linear and 1 minute polishing gives $\Delta z = 0.3 \, \mu m$ and 1 minute 40 seconds polishing gives $\Delta z = 0.8 \, \mu m$. Each time after removing a section, very light etching using Kroll etching solution was performed and optical micrographs were taken at both 200x and 500x magnification. Before the hardness indents disappeared completely, new ones were made in order to maintain continuity.

![Figure 3.14: Example of a region chosen for serial sectioning showing hardness indents for section alignment.](image)

3.2.4 EBSD and serial sectioning

As mentioned before, no special preparation was required for EBSD analysis, although, the samples were not etched for two reasons; etching gives problems of shadowing and oxidation of sample. For 3D EBSD, manual serial sectioning was carried out, each step followed by EBSD scans of the chosen regions. The EBSD scans were carried out on a Philips XL30 Environmental Scanning Electron Microscope (E-SEM) with a LaB$_6$ filament at Ghent University, Belgium. The scans were performed using an electron beam with an acceleration voltage of 25 kV and beam current of 53 $\mu A$. The working distance for all the EBSD scans was fixed at 22 mm and the scans were carried out at a tilt angle of 75°. The section thickness for 3-D EBSD was fixed at 0.8 $\mu m$, which is acceptably small as compared to the actual $\alpha$ grain size in order to prevent the loss of microstructural features. Due to the non etched state of the specimen, it was difficult to select the region for EBSD analysis using Secondary Electron Images (SEI) in tilted state of the specimen. Although Backscattered Electron Images (BEI) give very good contrast between $\alpha$ and $\beta$ grains due to significant solute partitioning, it is not feasible to take BEI images when trying for EBSD because the setup of the E-SEM does not allow rotation of sample to EBSD position without taking out the backscatter detector. This shortcoming proved to be one of the hindrances in choosing best regions to scan. Thus, polished samples were first etched, hardness indents made on regions of choice and then polishing was again carried out to remove any etching effects. Table 3.4 lists the EBSD scans and their characteristics. The penetration depth of electron beam in the sample in tilt position of 75° is around 25-30 nm. Due to presence of 5-15 nm thick oxide layer on surface of titanium, the pattern quality of EBSD scans for
titanium is generally quite low. During the scans, detection and calculation characteristics such as number of reflections, intensity of background correction, minimum and maximum number of detected bands, number of Hough peaks etc. were adjusted to get best possible indexation quality. The data collection was done with TexSEM Laboratories (TSL) Orientation Imaging Microscopy (OIM) Data Collection software ver. 4.6.

Table 3.4: Details of EBSD Scans. *- heat treatment given in Appendix A.

<table>
<thead>
<tr>
<th>Scan number(s)</th>
<th>Heat treatment #</th>
<th>Step size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>6</td>
<td>0.8</td>
</tr>
<tr>
<td>II-1</td>
<td>8</td>
<td>0.8</td>
</tr>
<tr>
<td>III-1 to III-32</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>IV-1, IV-2</td>
<td>16</td>
<td>0.5</td>
</tr>
<tr>
<td>V-1</td>
<td>35*</td>
<td>0.8</td>
</tr>
<tr>
<td>VI-1, VI-2</td>
<td>3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

3.2.5 EBSD data analysis
All the collected EBSD data was analyzed using TSL Orientation Imaging Microscopy (OIM) software ver. 4.6. Before analysis, the raw data has to be cleaned of mis-indexations, which can be done by using the cleanup tool of OIM. First step was “Grain Confidence Index Standardization” with grain tolerance angle set to 15° and minimum grain size set to 10 pixels. The next cleanup step was “Neighbor Orientation Correlation”. The following settings were used: grain tolerance angle- 15°, minimum confidence index- 0.3, cleanup level- 5. This procedure was chosen after trial and error with different settings. A tool for removing pseudosymmetry is also available, but this step is too much time consuming because each pseudosymmetric point has to be removed one by one. While checking the cleaned up scans, it was observed that quality of the maps was good even without pseudosymmetric corrections. The orientation and shapes of grains was clearly visible and thus pseudosymmetric correction was not carried out. During cleanup, however, proper care has to be taken not to remove useful points. For example, cleanup using “Neighbor Phase Correlation” tool resulted in the creation of artificial grains.

After cleanup, inverse pole figure (IPF), phase and image quality (IQ) maps were created with OIM for further analysis. The IPF maps can be used to show the orientations of different grains in different colors. The phase maps show contrast between different phases, not differentiating between grains of same phase but different orientation. The image quality maps give a quality of pattern for each point in grayscale format. For the creation of grain boundaries, misorientation between neighboring grains is calculated. For statistical reasons, OIM generates grain boundaries for misorientations greater than 2°. User defined misorientations can be used to identify different orientation relationships between different grains. Another useful tool in OIM is the creation of pole figures for specific directions. In order to validate misorientation calculations, pole figures for Burgers OR, i.e., [110], [111] and [112] directions for BCC and [0001], [1120] and [1100] directions for HCP were plotted.

3.2.6 WDS
For WDS, the samples were used in un-etched condition after final polishing step. Hardness indents procedure was applied in order to mark the regions to be scanned. Line scans were carried out on samples with a JEOL JXA 8900R microprobe. An electron beam with energy of 15 keV and a beam
current of 200 nA was used. The step size used varied with sample and will be given in Chapter 4 along with the results. CITZAF matrix correction program was employed to get elemental composition at each point. The elements Al, Fe, Mo, O and C were detected using the intensities obtained after correction. Ti was calculated as balance. The energy of the spectral lines, detection limit and counting error are given in Table 3.5.

Table 3.5: Energy (keV), detection limit (ppm) and counting error (wt. %) for each element analyzed with WDS.

<table>
<thead>
<tr>
<th>Element, X-ray line</th>
<th>Energy (keV)</th>
<th>Detection limit (ppm)</th>
<th>Counting error (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium, Al Kα</td>
<td>1.487</td>
<td>32</td>
<td>0.002</td>
</tr>
<tr>
<td>Iron, Fe Kα</td>
<td>6.403</td>
<td>117</td>
<td>0.004</td>
</tr>
<tr>
<td>Molybdenum, Mo La</td>
<td>2.293</td>
<td>192</td>
<td>0.011</td>
</tr>
<tr>
<td>Carbon, C Kα</td>
<td>0.282</td>
<td>-</td>
<td>0.004</td>
</tr>
<tr>
<td>Oxygen, O Kα</td>
<td>0.523</td>
<td>202</td>
<td>0.004</td>
</tr>
</tbody>
</table>

3.2.7 FIB 3D-EBSD

As discussed in § 3.1.3, the alignment of sample and ion gun in the SEM requires preparation of two perpendicular faces of the specimen. To achieve this, the cut half of the sample was polished using a special sample holder made of aluminium, which is softer than titanium and thus prevents problems during polishing. The 3D-EBSD analysis was carried out on a FEI Nova 600 Nanolab Dual Beam Focused Ion Beam (FIB) Field Emission Gun (FEG) Scanning Electron Microscope (SEM). The data collection was carried out using “Autoreveal” automatic data collection software for orientation contrast microscopy from FEI, which is based on the platform of Channel 6 HKL software. This software allows for automatic control of both FIB and EBSD, thus reducing human intervention to almost nil. In the process, alignment of the sample is done using two fiduciary marks made on the sample surface by the ion beam. An electron beam with 20 kV acceleration voltage and beam current of 2.4 nA was used for EBSD analysis. The working distance was fixed to 7 mm with a tilt angle of 7° and step size of 0.2 μm. The FIB used for sectioning had the following characteristics—Ga ion beam with 30 keV energy and 500 pA current. Total time for 69 sections was around 56 hours, which could also be altered by changing ion beam current. For the first 20 sections, interaction of the ion beam with the sample surface led to amorphization of the surface. An example of the amorphous surface of the sample is shown in Figure 3.15. For the other sections too, due to shape of the cavity created by ion milling and imperfect sample shape, reliable EBSD pattern was not obtained. However, the SEI images were good enough to be used to reconstruct one of the grains in the sectioned/analyzed area.
3-Dimensional Analysis of Microstructures in Titanium

3.2.8 3-D rendering

Optical micrographs were first post processed in Picasa. Etching with Kroll etching solution generally gives good visibility of α/β and α/α grain boundaries. β/β grain boundaries, however, are much harder to etch. Automatic brightness and contrast adjustments were made and each photo was converted to black and white in order to improve visibility of β/β grain boundaries. For 3D-EBSD, IPF maps were used. Images were imported into image analysis software Reconstruct. Although this software allows for automatic section alignment, it was not very accurate and thus manual alignment for each section was carried out using the hardness indents. During alignment, warpage correction was also carried out. This is very important when the successive layers are not parallel due to improper polishing. Section thickness for each section was separately defined by calculation of reduction in size of hardness indents. This operation takes into account the variations in section thickness due to complications in polishing. The automatic trace drawing tool called “Wildfire” in Reconstruct is a handy tool when all the sections have same contrast and brightness. However, tweaking of the parameters of wildfire tool still did not give satisfactory results. Thus, for each α grain, traces were drawn on each section using manual “Pencil” trace tool. The β/β grain boundaries were drawn using the “Draw Closed Point by Point” tool. For 3-D rendering, joining of traces was carried out using the “Boissonnat” algorithm inbuilt in Reconstruct. This algorithm allows for adequate representation of structures where branching is observed. To highlight the β/β grain boundaries in 3-D rendering, a different color was used and transparency of 70% was used.
Chapter 4 Results and discussion

4.1 General microstructure and EBSD

As mentioned in § 3.2.1, the transus temperature of the alloy under investigation is 800 °C. The bulk oxygen content of the alloy was calculated to be 0.2 wt% by fixing $T_p$ and other solute content of the alloy in Thermocalc. It must be emphasized that experimental determination of bulk oxygen content is very important due to oxygen’s significant contribution to changing the $T_p$ for titanium alloys. However, due to the ever present oxide layer on surface, it becomes very difficult to carry out exact surface oxygen content determination.

Microstructure evolution of the alloy was studied by a series of heat treatments at different temperatures with the same solutionizing treatment at 900 °C for ten minutes and is discussed below.

In the higher temperature range from 760 - 790 °C, the microstructure consists of $\alpha$ phase predominantly formed at or near some of the $\beta/\beta$ grain boundaries. This is shown in Figure 4.1. At somewhat lower temperatures (680 - 730 °C), almost all the $\beta/\beta$ grain boundaries are covered with $\alpha$ grains (Figure 4.2). In addition, many plate like $\alpha$ grains are seen in the vicinity of the $\beta/\beta$ grain boundaries, which are usually not connected to the grain boundary $\alpha$. Only a few $\alpha$ grains with a plate-like morphology can be observed in the $\beta$ grain interior. The fraction of this so called intragranular $\alpha$ increases as the temperature is lowered (Figure 4.3). Also, the $\alpha$ plates become more irregular in shape.

![Figure 4.1: Optical micrograph of a sample isothermally annealed at 760 °C for 15 hours.](image)
As the isothermal annealing temperature is lowered further (600 – 650 °C), the transformation changes from primary α to secondary α or bainite (Figure 4.4). These plates have a much different appearance than primary α and the size scales involved are also much smaller.
Results and discussion

Figure 4.4: Optical micrograph of sample isothermally annealed at 615 °C for one hour.

In order to analyze the orientation relationships between the α and β grains formed at different temperatures, EBSD scans were made. The EBSD scans are given in Figure 4.5 and Figure 4.6 for α formation at 760 °C, 730 °C and 680 °C, respectively. Rest of the EBSD scans with full grain boundary analyses are given in Appendix B.

Figure 4.5: IPF maps of (A) sample isothermally annealed at 760 °C for 15 hours (scan II-1); (B) sample isothermally annealed at 730 °C for 50 minutes (scan I-1). Grain boundaries with Burgers' orientation relationship are shown in black.
4.2 Optical 3-D analysis, 3-D EBSD and FIB 3D-EBSD
Heat treatment # 10 in Table 3.2 (solutionizing at 900 °C for ten minutes, isothermal annealing at 780 °C for 18 hours) was chosen for serial sectioning mainly because of the coarse morphology of α grains. An example of the microstructure of the sample is given in Figure 4.7.

Figure 4.7: Microstructure of heat treatment # 10 (solutionizing at 900 °C for ten minutes, isothermal annealing at 780 °C for 18 hours).
As seen in Figure 4.7, the microstructure consists of β grains, about 100 μm in diameter. Some α grains are present at β/β grain boundaries as well as inside the β grains. Analysis of 2-D micrographs, such as Figure 4.7, does not provide conclusive information about the morphology of α grains and it is hard to figure out the sites of nucleation and growth behavior. Therefore, 3-D analysis of the microstructures is required. Table 4.1 gives an overview of the 3-D analysis.

<table>
<thead>
<tr>
<th>Method</th>
<th>Regions studied</th>
<th>Number of sections per region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical serial sectioning</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>EBSD – serial sectioning</td>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>FIB – SEM</td>
<td>1</td>
<td>69</td>
</tr>
</tbody>
</table>

The results of serial sectioning with optical microscopy and EBSD have been divided into three main categories and these results will be presented and discussed below. The 3-D structures can be found on the supplementary CD. Transparent regions in 3-D reconstructions are β/β grain boundaries. Unless mentioned, the EBSD scans are for heat treatment # 10. All the EBSD scans are given in Appendix B. It was observed that Burgers’ OR is always followed between α and β grains. Some extra 3-D structures are given in Appendix C.

4.2.1 Branching
Branching was the most often observed mode of growth of α in the 3-D reconstructions. Figure 4.8 gives an example of a 2-D micrograph used for reconstruction in 3-D space. In the encircled region, three α particles lined up in a row can be seen. Also, there is a plate shaped α grain almost parallel to (but detached from) the β/β grain boundary. However, when 3-D reconstruction of the grains is carried out, as shown in Figure 4.9, it is seen that the α plate actually nucleated at a grain corner and grew first along β/β grain boundary and then inside the β grain. On the other hand, the three apparently individual α grains are actually connected as one α grain in 3-D space and this grain nucleated at a β/β grain boundary not visible in Figure 4.8. The α grain grew inside both β grains across the β/β grain boundary.

Figure 4.8: Optical micrograph of a region studied by serial sectioning. (Inset) un-rotated 3-D view of α grains in encircled region.
Another example of branching is illustrated in Figure 4.10 and Figure 4.11. In the 2-D optical micrograph (Figure 4.10), many α particles are present. The 3-D reconstruction of the region, given in Figure 4.11, shows that all these apparently individual α grains are actually connected in 3-D and form a single grain. This single α grain presumably nucleated at a β grain corner or at a β/β grain boundary. It grew not only along this grain boundary, but also along adjacent β/β grain boundaries and inside the β grain. The many α particles that are visible in Figure 4.10 result from branching of the α grain taking place while growing inside the β grain.
The next aspect of branching is shown in Figure 4.12 and Figure 4.13. The 2-D picture of Figure 4.12 seems to indicate that spheroidization of α grains took place, resulting in the particles A and B. However, the 3-D structure (Figure 4.13) shows that these particles are actually sections of two branches emanating from a single α grain. Nucleation of the grain appears to occur at the β/β grain boundary and the grain grows in a plate-like shape until it branches out, both along the β/β grain boundary and inside the β grain. The associated type of morphology in 2-D, the idiomorphic α grains lined up in a row, was observed in optical micrographs of all the samples studied.
In order to elucidate the mechanism of branching, serial sectioning followed by EBSD scans of each section was carried out. It was found that the orientation of both α and β grains did not change for different sections, which was expected as the sample was homogenized and undeformed. Two regions were chosen for analysis and henceforth they are referred to as regions 1 and 2 (scans III-6 to III-32 in Appendix B). Figure 4.14 gives IQ + IPF map of a section of region 1 studied by serial sectioning and EBSD. It is seen that the α grain grows along three different grain boundaries. When the α grain is reconstructed in 3-D (Figure 4.15), it can be seen that it branches out. The α grain also grows inside the β grain β1 and all the α branches have the same orientation (Figure 4.16).

The legend in Figure 4.14 shows the colors given to each orientation in the IPF map. This is the same for Figure 4.14, Figure 4.16, Figure 4.17 and Figure 4.20. Crystal orientations that are very close to each other are indicated with colors that are close in the color scheme. However, same colors do not necessarily imply that orientations are equal, since only one reference pole is given in the color scheme. For a full description of the crystal orientations by IPF maps, two IPF maps with a different reference system have to be constructed.
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Figure 4.14: Image quality (IQ) + inverse pole figure (IPF) map of section 1 of region 1 studied by serial sectioning – EBSD (scan III-5). (inset) un-rotated 3-D view of α grain in encircled region. The legend on right gives color scheme for the IPF map.

Figure 4.15: 3-D reconstruction of α grain in encircled region in Figure 4.14.

Figure 4.16: IQ + IPF map of section 11 of region 1 studied by serial sectioning – EBSD (scan III-15).
The other region selected for serial sectioning - EBSD is shown in Figure 4.17. It is seen that all the α particles inside a β grain, which were shown to be connected in 3-D (Figure 4.18) and represented by α1, have the same orientation. From Figure 4.17, it looks as if α1 has nucleated at the grain boundary between β1 and β3. However, a closer look at the 3-D reconstruction (Figure 4.18) presents a different picture. There is another α grain (α2, shown in blue color in Figure 4.18) on the other side of the β grain β1 which touches the branched α grain (α1). The misorientation between these two α grains was found to be about 3.5° (Figure 4.19 A), which might suggest that sympathetic nucleation had taken place. However, when orientation relationships were calculated, it was found that α1 had Burgers' OR with the β grain β1, whereas α2 had Burgers' OR with β grain β2. A possible explanation is that during early stages of transformation, two α nuclei formed at very close sites on the β/β grain boundary, each having Burgers' OR with opposite β grain across the grain boundary. Subsequent growth of the two α grains took place in opposite directions, resulting in the observed morphology. This is also confirmed by the fact that the two β grains have a low angle grain boundary between them, with a misorientation of about 4° (Figure 4.19 B). Figure 4.20 (A) and (B) show shapes of α1 and α2 grains in two other sections. α1 indeed reaches the grain boundary between β1 and β2 and could have nucleated there, grew inside grain β5 (which is below β1) and also along the grain boundary between β5 and β4.

Figure 4.17: IQ + IPF map of section 1 of region 2 studied by serial sectioning – EBSD (scan 311-20). (Inset) un-rotated 3-D view of α grains in encircled region.
Results and discussion

Figure 4.18: Rotated view of 3-D reconstruction of α grains in encircled region in Figure 4.17.

Figure 4.19: (A) <0001> pole figure of the two α grains in encircled region in Figure 4.17. (B) <111> pole figure of β1 and β2 grain in Figure 4.17.
The EBSD observations presented before show that all the α branches inside a single β grain have the same orientation, and thus are part of the same grain. This indicates that sympathetic nucleation has not taken place. However, the physical reasons for occurrence of interface instability cannot be derived from the present observations. Indirect proof for occurrence of interface instability can be seen from optical micrographs like Figure 4.21.

Another case of branching, observed in a different heat treatment, #16, Table 3.2 (solutionizing at 1050 °C for one hour and isothermal annealing at 760 °C for 18 hours) was revealed by the FIB 3D-EBSD experiment. Although EBSD data was lost due to surface amorphization, the SEI pictures were still good enough to be used for 3-D reconstruction. An example of the SEI images used for 3-D
reconstruction is shown in Figure 4.22 and the 3-D reconstruction of the \( \alpha \) grain is shown in Figure 4.23. It is seen from Figure 4.23 that the \( \alpha \) grain presumably nucleated at the \( \beta/\beta \) grain boundary and then grew in \( \beta \) grains on both sides of the boundary. Branching of the \( \alpha \) grain is also seen to occur and it changes its direction of growth for different branches.

![Figure 4.22: SEI image of a section milled using FIB used for 3-D reconstruction. The \( \alpha \) grain used for reconstruction is shown in the encircled region. Sample was solutionized at 1050 °C for one hour and isothermally annealed at 760 °C for 18 hours.](image1)

![Figure 4.23: 3-D reconstruction of the \( \alpha \) grain in encircled region in Figure 4.22.](image2)

An EBSD scan of the same microstructure, but a different region is shown in Figure 4.24.
The analysis of branched microstructures is a proof in itself of the complications that can arise when 3-D morphologies are not taken into account. For example, in variant selection studies, each particle that appears in a 2-D orientation map is taken as one grain. However, if the grains exhibit branching, then the 2-D microstructure would consist of a few apparent grains having the same orientation which, in reality, are part of the same grain. Thus, if 3-D morphologies are not studied, the frequency of occurrence of orientations would be overestimated. The other case relates to nucleation density analysis. Usually, nucleation density is calculated by counting the number of grains per unit area as seen in a 2-D micrograph. For example, in the encircled region in Figure 4.10, the number of α grains would be counted as 16, whereas it is clear from the 3-D reconstruction (Figure 4.11) that there is only a single α grain. This also means that fitting of experimental 2-D nucleation density data to models for prediction of microstructure evolution could result in a considerable error.

Based on the results from both 3-D and orientation data, it is now clear that there exists no misorientation (or α/α grain boundary) between α at the β/β grain boundaries (αGB) and the α branches (αWGB). In view of this, the classification of primary α into grain boundary α and Widmanstätten α is not correct. However, it must be mentioned that 3-D analysis of α plates formed at lower temperatures might yield different results, mainly because, according to the definition of sympathetic nucleation, the probability of occurrence of sympathetic nucleation increase when the transformation temperature decreases due to increased supersaturation.
4.2.1.1 *Widmanstätten morphology - a special case of branching*

α grains similar to Widmanstätten needles in steels\textsuperscript{55} were also observed in the 3-D reconstructions. Figure 4.25 shows a 2-D micrograph of a section used for 3-D reconstruction. However, the exact morphology of the α grain is not clear from Figure 4.25. It looks as if sympathetic nucleation or spherodization has taken place. When the α grain is visualized in 3-D space (Figure 4.26), it is seen that the α grain has a needle shaped morphology, similar to the one observed in steel. Also, the separate α particles visible in the encircled region (Figure 4.25) are actually part of a single grain. The α grain, nucleated presumably at the β/β grain boundary, grows inside the β grain in a needle shape. This case is just a special case of branching, one in which the growth direction of α inside the β grain has a very high angle with the β/β grain boundary.

![Figure 4.25: Optical micrograph of a region studied by serial sectioning.](image)

The next example of Widmanstätten morphology is given in Figure 4.27. The α particle in the encircled region looks like a plate growing along a β/β grain boundary. However, as seen from the 3-
D reconstruction, the $\alpha$ grain grows along the adjacent $\beta/\beta$ grain boundary and also inside the $\beta$ grain, resulting in needle shaped morphology.

Figure 4.27: (A) Optical micrograph of a section. (B) Un-rotated view of 3-D reconstruction of the $\alpha$ grain highlighted in (A).

In order to compare the Widmanstätten observed in the current project with Widmanstätten in steels, as reported by Spanos, 35 EBSD scans were performed on similar regions. Figure 4.28 shows IPF maps of two regions exhibiting Widmanstätten type morphology. Although it is probable that these grains might be connected in 3-D, it was not possible to carry out 3-D EBSD in these regions due to experimental difficulties. It is clearly seen that unlike for the case of Spanos et al., 35 where they observed a misorientation of 5-10° from end to end of the needles, there exists no misorientation within the Widmanstätten needles for this case. Also, unlike for the case of steel, big colonies of needles or plates were not observed for this heat treatment. However, Widmanstätten colonies were observed for heat treatments with lower isothermal holding temperatures.
4.2.2 Zigzag morphology

In many micrographs, a so called zigzag morphology has been observed, which seems to be more common at lower temperatures. A typical example of this morphology, consisting of a β/β grain boundary bending between α grains or branches, is seen in Figure 4.29. This type of morphology has been reported previously for titanium alloys, and different formation mechanisms were suggested. In Ref. [25], it was postulated that nucleation of separate α laths takes place with the laths having an orientation relation with one of the two β grains across the grain boundary. Subsequent growth of these laths in order to maintain the orientation relationship leads to the formation of this type of morphology. In Ref. [62], it was proposed that this morphology forms according to the so called ‘Pucker’ mechanism, in which bending of β/β grain boundary occurs in order to orient the α grain with respect to one of the β grains, while growth occurs in the opposite β grain, thus resulting in the observed zigzag structure. Both these models were based on 2-D observations only.

Based on the 3-D reconstructions (Figure 4.30) of the structure in Figure 4.29, a different mechanism is proposed. It is seen that the different α particles in the optical micrograph are actually manifestations in 2-D of a single, branched α grain. Thus, this structure is essentially caused by branching of the α grains, involving concurrent movement of the β/β grain boundaries which reduce their interfacial energy by repositioning in order to have the lowest surface area between two α branches. This observation was further corroborated by the EBSD scan carried out on a similar region (Figure 4.31), which shows that the α particles in the zigzag structure all have the same orientation.
Figure 4.29: Example of microstructure with zigzag morphology.

Figure 4.30: 3-D reconstruction of α grains in Figure 4.29. (A) Un-rotated view. (B) Rotated view of 3-D reconstruction for better visualization.
Further analysis of the EBSD scan reveals that the $\beta$ grains on both sides of the grain boundary have an orientation difference for two (110) planes that is less than 5° (Figure 4.32). The pole figures of the $\alpha$ grain are shown in Figure 4.33. The (0001) plane of the $\alpha$ grain is almost parallel to both the (110) planes of the $\beta$ grains. In fact, the $\alpha$ grain has Burgers’ orientation relationship with both $\beta$ grains, with misorientation angle of about 2°. This is shown by superimposing the pole figures of $\alpha$ and both the $\beta$ grains, Figure 4.34.
Figure 4.32: [110], [111] and [112] pole figures for grains $\beta_1$ and $\beta_2$ in Figure 4.31. Encircled region highlights the common (110) plane for the two $\beta$ grains.

Figure 4.33: [0001], [1120] and [1100] pole figures for particles $\alpha_1$, $\alpha_2$ and $\alpha_3$ in Figure 4.31.
Figure 4.34: Superimposed pole figures from Figure 4.32 and Figure 4.33. Green points are for the α particles, blue points are for the β grain β1 and red points are for the β grain β2 in Figure 4.31. (A) \([0001]_{hcp} \parallel [110]_{bcc}\), (B) \([1120]_{hcp} \parallel [111]_{bcc}\), (C) \([1100]_{hcp} \parallel [11ar{2}]_{bcc}\).

It is interesting to note from combination of Figure 4.32 and Figure 4.33 that although β1 and β2 share the same [110] direction with [0001] direction of the α grain, the two β grains do not share the same [111] and [112] directions with [1120] and [1100] directions, respectively, of the α grain.

A modification of the ‘Pucker’ mechanism is proposed to explain the observations, shown schematically in Figure 4.35. In this case, the α nucleus forms at the β/β grain boundary, having Burgers’ orientation relationship with both the β grains, with a small misorientation, if required. The growth of this nucleus takes place in such a way that the longer faces of the α grain are low-energy interfaces with respect to both β grains. The interfacial aspect for this case is discussed later. During growth of the α grain, motion of β/β grain boundary will take place in order to minimize total interface energy. Depending on the angle between the growth direction of α grain and the initial β/β grain boundary, one of the following two cases can occur. If the angle is smaller than a limiting angle, the α grain can grow without any bending of the β/β grain boundary (low angle, position 1 in Figure 4.35). But, if the angle is higher at some other height in the β/β grain boundary, branching of the α grain and subsequent bending of the boundary takes place (low angle, position 2 in Figure 4.35). Unlike the β/β grain boundary, the triple edge limiting the grain boundary between the β grains is immobile. In order to compensate for this, change in growth direction of the α grain takes place in cases where the angle between the growth direction of the α grain and the prior β/β grain boundary is high, resulting in a morphology as shown in the high angle, after growth case in Figure 4.35. The α grain can also branch out at some other height in the β/β grain boundary, if the angle between the α
growth direction and \( \beta/\beta \) grain boundary becomes even higher, resulting in a morphology similar to the one shown in the encircled region in Figure 4.31.

The limit of the angle between the \( \alpha \) grain growth direction and the \( \beta/\beta \) grain boundary is given by the equation:

\[
\tan \theta = \frac{W}{L} = \frac{1}{\eta} \quad \text{(eq. 4.1)}
\]

where \( \theta \) is the angle in question, \( W \) is the width and \( L \) is the length of the \( \alpha \) grain. A schematic of this is shown in Figure 4.36. The value \( \frac{W}{L} \) is equal to the inverse of the aspect ratio (\( \eta \)) of the \( \alpha \) grain. \( \frac{W}{L} \) can also be interpreted as the ratio of mobilities of long and short interfaces of the \( \alpha \) grain, as defined in the Wulff's diagram concept.\(^{66}\)
Results and discussion

Figure 4.36: Schematic of limiting value of $\theta$. (A) Full view. (B) Prior $\beta/\beta$ grain boundary superimposed on $\alpha$ grain in order to highlight definition of $\theta$.

It must be mentioned that while branching occurs presumably due to interface instability, zigzag morphology is a result of orientation constraints.

Interfacial Considerations

As discussed in § 2.2.5.5, previous studies using TEM have indicated that the interface between $\alpha$ and $\beta$ grains has a ledged structure. The interface plane is along the lattice invariant line $[335]_\beta$ direction, along which transformation strain is absent. The ledges are formed in such a way that the $(11\bar{2})$ plane of $\beta$ grain forms the ledge face. This means that the macroscopic interface should be at an angle of $14.4^\circ$ from the ledge plane, $(11\bar{2})$. This explanation is widely accepted. However, while analyzing the zigzag structure in Figure 4.31, it was found that the $(1\bar{1}00)$ plane of the $\alpha$ grain, which is parallel to the $(1\bar{1}00)$ plane of the $\beta$ grain, was actually parallel to the interface and not at an angle of $14.4^\circ$. It has also been reported previously that the interplanar spacing of $(0002)_\alpha$ almost matches the interplanar spacing of $(110)_\beta$. These two planes, which form the basis of Burgers' orientation relationship, are perpendicular to the corresponding $(1\bar{1}00)_\alpha$ and $(11\bar{2})_\beta$ planes. Thus it might mean that atomic matching, at an interface formed when the $(0002)_\alpha$ and $(110)_\beta$ are perpendicular to the interface, is very good. In order to investigate this, atomic models were first made with ping-pong balls and later constructed with JSV software. 3-D reconstructions of the interface are given in Figure 4.37 and Figure 4.38. It was found that every alternate row of atoms at the interface matched exactly, with the atoms in the row between being displaced about 24% from the optimum position. This condition is energetically more favorable than that for an interface in which $(0002)_\alpha$ and $(110)_\beta$ are parallel to the interface, similar to the interface observed in BCC and FCC transformations. The latter case results in a highly irregular atomic arrangement at the interface, in which every 36th atom has a perfect matching and rest of the atoms are displaced by a significant amount. The relatively better matching of atoms in the case shown in Figure 4.37 and Figure 4.38 is allowed by the ABAB... stacking in both BCC and HCP structures and by the equal distances of the two sets of lattice planes.
4.3 Effect of homogenizing treatment

In order to study the effect of homogenizing treatment on microstructure of the alloy, heat treatments at two different solutionizing temperatures (900 °C, 1050 °C) were done. Keeping the isothermal annealing time and temperature same, different solutionizing treatments were carried out to compare different features of the transformation. In most metal alloys, it is observed that if the grain size of a material increases, the total nucleation density per unit volume or area decreases due to decreased area of grain boundaries per unit volume, which are the preferred sites for
nucleation.\(^6\) It will be shown that titanium does not conform to other metals in this respect. The different experiments have been divided into two categories, discussed below.

4.3.1 Similar \(\beta\) grain size, short annealing times

Heat treatments at 1050 °C for short times and at 900 °C for longer times (see Table 3.2) were carried out to get almost the same \(\beta\) grain size. The annealing temperature for \(\beta\) to \(\alpha\) transformation was 730 °C and the annealing time was 50 minutes. Figure 4.39 and Figure 4.40 show an example of such an experiment. For the sample heat treated at 900 °C for ten minutes, \(\alpha\) forms primarily along most of the \(\beta/\beta\) grain boundaries. A few \(\alpha\) nuclei can also be seen inside the \(\beta\) grains, but are very few in density. However, the sample solutionized at 1050 °C for 20 seconds exhibits a very different kind of transformation. Although \(\alpha\) formation along the \(\beta/\beta\) grain boundaries is still seen, much higher fraction of plates growing inside the \(\beta\) grains is observed. Also, nucleation density at grain boundaries is much higher for the sample solutionized at 1050 °C than the sample solutionized at 900 °C.

Figure 4.39: Optical micrograph of sample solutionized at 900 °C for ten minutes and isothermally annealed at 730 °C for 50 minutes.
Similar treatments for longer solutionizing times exhibit even stranger effects. Figure 4.41 shows the optical micrograph of a sample solutionized at 900 °C for six hours. The β grain size of the material has increased considerably and formation of α is again primarily at the β/β grain boundaries. But there is a greater tendency for formation of plates growing into the β grains, although they appear to have grown from the grain boundary. In case of the sample solutionized at 1050 °C for one hour (Figure 4.42), even higher number of α grains growing into the β grains is observed. However, one difference between the samples solutionized at 900 °C for ten minutes and six hours is that higher number of nuclei per unit β/β grain boundary length is seen for longer solutionizing time.
Figure 4.42: Optical micrograph of sample solutionized at 1050 °C for one hour and isothermally annealed at 730 °C for 50 minutes.

Figure 4.43 shows an optical micrograph of a sample heat treated at 900 °C for 36 hours. It can be seen that all the β/β grain boundaries are covered with α grains with a high nucleation density. There is a high density of α plates growing inwards from the grain boundary α and also colonies of α plates nucleated intragranularly. Intragranular nucleation is evident from the fact that the size scale of the α plates is much smaller than the distance from the β/β grain boundaries and the probability of the α plates, in middle of the β grains, growing from a β/β grain boundary is very low. These colonies of α were also seen close to the edge of the sample solutionized at 900 °C for six hours (Figure 4.44 A), although, this is much more pronounced for the case of the current sample (Figure 4.44 B). Also, the fraction of α transformed for the case of 900 °C for 36 hours is much more than any of the other solutionizing treatments at 900 °C or 1050 °C for shorter times, with the same isothermal annealing treatment.

Figure 4.43: Optical micrograph of sample solutionized at 900 °C for 36 hours and isothermally annealed at 730 °C for 50 minutes.
Figure 4.44: Optical micrographs of edge of samples solutionized at 900 °C for (A) six hours; (B) 36 hours.

Figure 4.45: Optical micrograph of sample solutionized at 1050 °C for 6 hours and isothermally annealed at 730 °C for 50 minutes.

Figure 4.45 shows an optical micrograph of the sample heat treated at 1050 °C for 6 hours. The microstructure in this case is similar to the sample solutionized at 1050 °C for one hour (Figure 4.42). Although the β grain size is similar to the sample homogenized at 900 °C for 36 hours (Figure 4.43), there are no intragranular α plates present. The α plate morphology at the grain boundaries is also different for the two cases.

For the samples solutionized at 900 °C for any amount of time, higher fraction of α was always observed close to the edge, which could be attributed to the presence of oxide rich layer close to the surface. However, for the samples solutionized at 1050 °C, this edge effect was not observed. This case is shown in Figure 4.46. Figure 4.46 (A) shows much higher fraction of α in a region from the edge till about 70 – 80 μm inside after solutionizing at 900 °C. However, Figure 4.46 (B) shows that after solutionizing at 1050 °C there is no difference between the edge regions as compared to the
bulk, with only a few α plates growing inside from the edge. One explanation for this behavior might be that oxygen from the surface diffuses into the bulk due to the higher temperature. But, calculations for diffusion distances indicate that at 900 °C, oxygen atoms would be able to diffuse about 4 μm in ten minutes, whereas at 1050 °C, this diffusion distance is only 12.5 μm for one hour. Clearly these distances are much higher than the observed high transformation region in Figure 4.46 (A). Also this does not explain why a difference between surface and bulk is observed for the samples solutionized at 900 °C for longer times (compare Figure 4.41, Figure 4.43 and Figure 4.44), involving similar diffusion distances. Although there might exist a difference between oxygen solubility in titanium at 900 °C and 1050 °C which might be responsible for this effect, no references could be found in the literature which support this.

![Figure 4.46: Optical micrographs of edge of samples solutionized at (A) 900 °C for ten minutes; (B) 1050 °C for one hour.](image)

### 4.3.2 Similar β grain size, long annealing times

In order to check the influence of solutionizing temperature and time on the equilibrium fraction of α, heat treatments were carried out with isothermal annealing at 760 °C for 18 hours. Calculations using Thermocalc predict 8.35% of α to be transformed at 760 °C under equilibrium. The sample solutionized at 900 °C for ten minutes (Figure 4.47) has a fraction of α close to the predicted equilibrium value. However, the sample solutionized at 1050 °C for 30 seconds (Figure 4.48) has a higher fraction of α transformed than the predicted equilibrium value of about 8.5%, although the β grain size is almost the same.
Solutionizing at longer times at 900 °C and 1050 °C was also carried out. The sample solutionized at 900 °C for six hours (Figure 4.49) has a higher fraction of α than the predicted equilibrium fraction. The sample solutionized at 1050 °C for one hour (Figure 4.50) has even higher fraction transformed of α.
Figure 4.49: Optical micrograph of sample solutionized at 900 °C for six hours and isothermally annealed at 760 °C for 18 hours.

Figure 4.50: Optical micrograph of sample solutionized at 1050 °C for one hour and isothermally annealed at 760 °C for 18 hours.

There exists no explanation in literature which deals with this kind of behavior. The observation that transformation product more than equilibrium fraction is formed has not been investigated before, not at least for complex multi-component titanium alloys. One possible explanation for the high fraction of α might be that solute redistribution takes place during solutionizing, which can shift the equilibrium and the transus temperature $T_p$. However, this cannot explain why there is a difference between the samples solutionized at 900 °C and 1050 °C, even when the grain size is the same. Even if the equilibrium is shifted due to solute redistribution, which itself is highly unlikely at the high temperatures studied, it should change by the same amount for same diffusion distances, which is
implied by the same grain size. More experiments need to be done to investigate the possible underlying mechanisms responsible for this kind of behavior. One possibility is the formation of martensite prior to transformation, discussed later in § 4.5, which can act as nucleation sites for $\alpha$ grains. However, the investigation of martensite formation temperature in itself is very difficult. Another explanation might be that the equilibrium calculations from Thermocalc are not correct, as discussed in § 4.4.1 and § 4.4.2.

4.4 Elemental analysis

Elemental analysis of the $\alpha$ and $\beta$ grains is important for a complete understanding of the mechanism of formation of the transformation product, $\alpha$. As described in § 2.2.5.3, transformation to primary $\alpha$ is considered as a nucleation and growth process, fully diffusion controlled. This means that the $\alpha$ which forms during heat treatment should have equilibrium concentration of solute elements at all times during and after the transformation. The equilibrium value (from Thermocalc) of solute elements in $\alpha$ and $\beta$ phases at different temperatures is given in Table 4.2.

Table 4.2: Equilibrium concentration of different solute elements in $\alpha$ and $\beta$ phases at different temperatures (from Thermocalc).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Al (wt%)</th>
<th>Fe (wt%)</th>
<th>Mo (wt%)</th>
<th>O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\alpha$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>780</td>
<td>2.12</td>
<td>1.47</td>
<td>0.075</td>
<td>4.75</td>
</tr>
<tr>
<td>735</td>
<td>2.11</td>
<td>1.36</td>
<td>0.11</td>
<td>5.53</td>
</tr>
<tr>
<td>730</td>
<td>2.10</td>
<td>1.35</td>
<td>0.12</td>
<td>5.64</td>
</tr>
<tr>
<td>700</td>
<td>2.07</td>
<td>1.28</td>
<td>0.13</td>
<td>6.16</td>
</tr>
</tbody>
</table>

It can be seen from Table 4.2 that although Fe, Mo and O partition to a considerable extent across $\alpha$ and $\beta$, Al partitioning is much less pronounced. In order to check the solute concentrations in $\alpha$ and $\beta$, elemental analysis was carried out employing WDS. The results have been divided according to isothermal annealing temperature and will be discussed in the text that follows.

4.4.1 Isothermal annealing at 780 °C

In order to study the composition of primary $\alpha$ formed at high isothermal annealing temperatures and long times, WDS line scans (step size – 0.5 µm) were carried out on a sample solutionized at 900 °C for ten minutes and then isothermally annealed at 780 °C for 18 hours (heat treatment # 10). Figure 4.51 shows the location and direction of the line scans. Results of the line scan 1 are given in Figure 4.52.
Results and discussion

Figure 4.51: Optical micrograph showing location and direction of line scans carried out for elemental analysis (solutionizing at 900 °C for ten minutes, isothermal annealing at 780 °C for 18 hours). Dashed lines indicate the location of β/β grain boundaries and arrow tails indicate beginning location and arrow heads indicate ending location of the line scans.

Figure 4.52: Concentrations of different elements along line 1 in Figure 4.51.

The scan shows that although Fe and Mo have the concentration in α as predicted by Thermocalc, Al behavior is different from Fe and Mo. Also, whereas Fe content in β is lower than predicted by
Thermocalc, Mo in $\beta$ is higher. This indicates that the equilibrium content of Al in $\alpha$ and Fe and Mo in $\beta$ predicted by Thermocalc is ‘wrong’. Based on this observation and assuming that the concentration of an element just ahead of the $\alpha/\beta$ interface on the $\beta$ side is the equilibrium composition, it is proposed that the Al, Fe and Mo composition of $\alpha$ grains for line scan 1, shown in Figure 4.52, are the actual equilibrium values and similarly for the $\beta$ phase. The concentration of Mo in the $\beta$ phase, just ahead of the interface, for the other line scans (Figure 4.54, Figure 4.55, Figure 4.56, Figure 4.57 and Figure 4.58) was also considered in evaluating the equilibrium Mo content. The experimental equilibrium concentrations for $\alpha$ and $\beta$ phases are given in Table 4.3. Figure 4.53 shows the results of line scan 1 in Figure 4.51 along with the experimental equilibrium values.

Table 4.3: Experimental equilibrium concentration of different alloying elements in $\alpha$ and $\beta$ phase at 780 °C.

<table>
<thead>
<tr>
<th></th>
<th>Al (wt%)</th>
<th>Fe (wt%)</th>
<th>Mo (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Alloy content predicted by Thermocalc</td>
<td>2.12</td>
<td>1.47</td>
<td>0.075</td>
</tr>
<tr>
<td>Alloy content from experiments</td>
<td>2.49</td>
<td>1.42</td>
<td>0.093</td>
</tr>
</tbody>
</table>

Figure 4.53: Concentrations of different elements along line 1 in Figure 4.51. Also shown are the experimental equilibrium values.

The results of line scans 2A, 2B, 3A, 3B and 4 are given in Figure 4.54, Figure 4.55, Figure 4.56, Figure 4.57 and Figure 4.58, respectively.
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Figure 4.54: Concentrations of different elements along line 2A in Figure 4.51.

Figure 4.55: Concentrations of different elements along line 2B in Figure 4.51.
Figure 4.56: Concentrations of different elements along line 3A in Figure 4.51.

Figure 4.57: Concentrations of different elements along line 3B in Figure 4.51.
Figure 4.58: Concentrations of different alloying elements along line 4 in Figure 4.51. Because the α grain was curved and the line scan was made along a straight line, the apparently high Fe and Mo content inside the α grain can be attributed to some X-ray signal coming from β grain underneath.

One interesting aspect to note here is that for lines 1, 2A, 2B, 3A and 3B, whereas Al and Fe distribution in β is uniform, Mo still has a gradient in concentration showing solute buildup at the interface. Although 18 hours at 780 °C is enough for Mo to diffuse around 85 μm (this value can vary based on calculation of diffusion coefficient reported by different authors), this gradient over a distance of 10 μm means that the α grains in lines 2 and 3 did not nucleate at the start of isothermal annealing. However, if the other diffusion data are considered, 18 hours at 780 °C means a diffusion distance of only 2.5 μm, meaning that there is not enough time for complete diffusion of Mo atoms. Due to the discrepancy in diffusion data, there are two possible explanations: either Mo diffusion is still not complete after 18 hours and/or the α grains have nucleated at a later stage in the transformation. Also, the higher Fe and Mo content in the two α grains supports the latter explanation. The profile in Mo concentration in β phase also means that there is still a driving force for transformation. It was observed that the phase fraction of α did not change in samples isothermally annealed for more than ten hours. This means that macroscopically equilibrium might have been achieved, but, changes at microscopically local level can still occur. However, experimental validation of this is not possible because it would require an in-situ study of coarsening of a few α grains.

Because grain boundaries are relatively open structures as compared to the bulk, diffusion along the grain boundaries is generally considered to be faster. Line scans 2A, 2B and 3A, 3B were used to compare the concentration profiles of different elements ahead of the α/β interface along both the β/β grain boundaries and inside the β grains. Figure 4.54 and Figure 4.56 correspond to line scans made along β/β grain boundaries and; Figure 4.55 and Figure 4.57 correspond to line scans made to study the elemental distribution inside β grains. Although diffusion of Al and Fe could not be studied,
comparison of Figure 4.54 and Figure 4.55 shows that the concentration profile of Mo is the same for along a β/β grain boundary and inside a β grain. Figure 4.56 and Figure 4.57 also yield similar results. This might mean that the rate of diffusion of Mo along the grain boundary is same as inside the bulk.

4.4.2 Isothermal annealing at 735 °C
Elemental analysis was carried out on a sample solutionized at 900 °C for ten minutes and isothermally annealed at 735 °C for 12 hours. The location and direction of the line scans is given in Figure 4.59. Step size used was 0.25 μm. The results for line 1 are given in Figure 4.60.

Figure 4.59: Location and direction of line scans carried out for elemental analysis (solutionizing at 900 °C for ten minutes and isothermal annealing at 735 °C for 12 hours). Arrow tails indicate beginning location and arrow heads indicate end location.

Figure 4.60: Concentrations of different elements along the line scan 1 in Figure 4.59.
It is seen that for line scan 1 (Figure 4.60), that is, the α grain along the grain boundary, Fe and Mo have almost reached the equilibrium value predicted by Thermocalc. Once again Al partitioning is more than predicted by Thermocalc. In analogy to the approach in § 4.4.1, the equilibrium concentrations of different solute elements in α and β phases were reevaluated and are given in Table 4.4. Figure 4.61 shows the results for line scan 1 in Figure 4.59 along with the experimental equilibrium concentrations.

**Table 4.4: Experimental equilibrium concentration of different alloying elements in α and β phase at 735 °C.**

<table>
<thead>
<tr>
<th></th>
<th>Al (wt%)</th>
<th>Fe (wt%)</th>
<th>Mo (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>β</td>
<td>α</td>
</tr>
<tr>
<td>Alloy content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>predicted by</td>
<td>2.11</td>
<td>1.36</td>
<td>0.11</td>
</tr>
<tr>
<td>Thermocalc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy content</td>
<td>2.3</td>
<td>1.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>
4.4.3 Equilibrium Calculations

Based on the observations from § 4.4.1 and § 4.4.2, the phase diagrams were reevaluated and the equilibrium concentrations of α and β at 780 °C and 735 °C are given in Figure 4.63, Figure 4.64 and Figure 4.65. It is seen that the experimental equilibrium values for Al are very different than the ones from Thermocalc, both for the α and β phases. However, the Fe and Mo concentrations in α, both predicted from Thermocalc and from elemental analysis, match very well. The Fe and Mo concentrations in β phase from Thermocalc, however, do not agree with the calculated equilibrium values. This is because the equilibrium phase fraction predicted from Thermocalc is also different from observations, already mentioned in § 4.3.2.
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Figure 4.63: Phase diagram showing equilibrium concentration of Al at 780 °C and 735 °C, as calculated from Thermocalc and from elemental analysis.

Figure 4.64: Phase diagram showing equilibrium concentration of Fe at 780 °C and 735 °C, as calculated from Thermocalc and from elemental analysis.
It is important to point out a few problems with the results given above. Firstly, it is seen that the molybdenum composition in $\alpha$ at 780 °C is higher than what Thermocalc predicts. This is in keeping with the observation that $\alpha$ phase fraction observed experimentally was higher (around 10 %) than predicted by Thermocalc (5.5 %), which means more Mo and Fe rejection into $\beta$ takes place than what is predicted. If, in fact, rejection of $\beta$ stabilizers into $\beta$ was higher than the predicted, it would mean that the Fe concentration in $\beta$ at 780 °C should also be higher than the Thermocalc value. However, this is not the case, as seen from Figure 4.64, where Fe content in $\beta$ is 4.62 wt% at 780 °C and not 5.05 wt%, which should be the Fe content for 10 % $\alpha$ fraction. Currently it is not possible to explain this discrepancy. Secondly, the experimental Mo content in $\beta$ at 735 °C (7.9 wt%) is only marginally higher than that at 780 °C (7.83 wt%). However, the phase fraction of $\alpha$ at 735 °C (around 20 %) is higher than at 780 °C (10 %), which means that the extra $\alpha$ formed has rejected very little amount of Mo into the $\beta$ phase. If the phase fraction of about 20 % $\alpha$ at 735 °C is considered, equilibrium Mo content in $\beta$ should be 8.6 wt%. This might be explained by saying that the Mo in $\alpha$ and $\beta$ grains in line 1 in Figure 4.59 has not reached equilibrium yet.

4.4.4 Isothermal annealing at 730 °C
Elemental analysis for two samples isothermally annealed at 730 °C for 50 minutes, but having different solutionizing treatments, was carried out. Step size used was 1 μm.

4.4.4.1 Solutionizing at 900 °C for ten minutes
The location and direction of line scans for the first sample, solutionized at 900 °C for ten minutes is given in Figure 4.66. Two line scans were made. One was made along a $\beta/\beta$ grain boundary with transformed grain boundary $\alpha$ and another along a $\beta/\beta$ grain boundary without transformation. For this sample, oxygen measurement was also carried out. Results of composition analysis for lines 1 and 2 are shown in Figure 4.67 and Figure 4.68, respectively. It can be seen that for line 1, that is, through grain boundary $\alpha$, partitioning of Al, Fe, Mo and O takes place, although none of the alloying
Results and discussion

...elements reaches the equilibrium both in \( \alpha \) and \( \beta \) (as predicted by Thermocalc). Also, the oxygen content in the two \( \beta \) grains is different, an observation attributable to \( \beta \) grain orientation dependence of oxide layer.

Figure 4.66: Location and direction of line scans carried out on sample solutionized at 900 °C for ten minutes and isothermally annealed at 730 °C for 50 minutes. Arrow tails indicate beginning location and arrow heads indicate end location.

Figure 4.67: Concentrations of different alloying elements along line scan 1 in Figure 4.66.
The results for line 2 (Figure 4.68) indicate that there is no difference in solute concentration at the β/β grain boundary and the grain interior. The difference in oxygen content of the two β grains can again be attributed to difference in oxide layer thickness for different β grain orientation. It is obvious that the reason that no transformation takes place at the β/β grain boundary is not inhomogeneous solute distribution, but might be related to β grain orientation dependent character of the β/β grain boundaries. Detailed EBSD analysis is required to explain this effect.

### 4.4.4.2 Solutionizing at 1050 °C for one hour

The second sample analyzed was solutionized at 1050 °C for one hour and isothermally annealed at 730 °C for 50 minutes. Figure 4.69 gives the location and direction of the line scans.
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Again, two line scans were carried out. One line scan was made along a β/β grain boundary having grain boundary α and a few Widmanstätten plates. The other line scan was made at a β/β grain boundary having no transformation. The results of composition analysis for line 1 and 2 are given in Figure 4.70 and Figure 4.71.

Figure 4.70: Concentrations of different alloying elements along line scan 1 in Figure 4.69.

Figure 4.71: Concentrations of different alloying elements along line scan 2 in Figure 4.69.
It can be seen that for the case of grain boundary $\alpha$ (Figure 4.70), the results match the results for the sample having a different solutionizing treatment but the same annealing treatment (Figure 4.67). This means that partitioning of the alloying elements depends on the annealing treatment and not on solutionizing. This, however, does not explain why different nucleation and morphological characteristics of $\alpha$ phase are observed for different solution treatments (compare, for example, Figure 4.39 and Figure 4.42). Also, unlike for the case of solutionizing at $900$ °C for 10 minutes, the oxygen analysis does not show any composition difference between $\beta$ grains. But, the results from only four scans are not enough to fully understand the actual behavior of oxide layer. Results of the line scans given in Figure 4.67 and Figure 4.70 show that the concentrations of Fe and Mo in $\beta$, just ahead of the interface, are not equal to the calculated equilibrium value.

4.4.5 Isothermal annealing at $700$ °C

Elemental analysis was carried out on two samples with same solutionizing treatment at $900$ °C for ten minutes. Step size used was 0.5 μm. Location and direction of line scans of the first sample, isothermally annealed at $700$ °C for 30 minutes, is shown in Figure 4.72. The results of composition analysis for lines 1 and 2 are shown in Figure 4.73 and Figure 4.74, respectively. It can be seen that for both lines 1 and 2, all the alloying elements do not reach the equilibrium values predicted by Thermocalc. The deviation from equilibrium concentrations for Mo is much more than that for Fe. Also, the alloying element concentrations in $\alpha$ phase are much closer to equilibrium for the case of line 2 than for line 1. This might be attributed to the fact that for line 1, a lot of $\alpha$ plates are present close to each other, meaning that solute rejection into the $\beta$ phase becomes more and more difficult during growth due to solute buildup, which can be seen from the difference in peak Mo and Fe content in line 1 and line 2.

Figure 4.72: Location of line scans carried out on sample solutionized at $900$ °C for ten minutes and isothermally annealed at $700$ °C for 30 minutes.
Results and discussion

Location and direction of line scans in the second sample, isothermally annealed at 700 °C for two hours is shown in Figure 4.75. The results of composition analysis for lines 1 and 2 are given in Figure 4.76 and Figure 4.77, respectively. It can be seen that although for both lines 1 and 2, Fe and Mo do not reach the predicted equilibrium concentrations in α, Al has partitioned more than equilibrium...
concentration, according to Thermocalc. This observation is similar to § 4.4.1 and § 4.4.2. Thus, it can be said that the equilibrium concentrations predicted by Thermocalc are not correct for 700 °C too. As compared to the sample isothermally annealed at 700 °C for 30 minutes, this sample has Mo and Fe concentrations in α much closer to equilibrium. Again, due to slower diffusion of Mo, deviation from equilibrium is more for Mo than for Fe.

Figure 4.75: Location and direction of line scans carried out on sample solutionized at 900 °C for ten minutes and isothermally annealed at 700 °C for two hours.

Figure 4.76: Concentrations of different alloying elements along line scan 1 in Figure 4.75.
4.4.6 Summary of elemental analysis
All the results presented in § 4.4.1 - 4.4.5 indicate that the transformation from β to primary α is certainly not of purely diffusion controlled character (case in which equilibrium concentrations are always maintained at the interface at all transformation times). During the initial stages of transformation, α formation takes place with a composition far away from equilibrium composition. Also, local equilibrium in the β phase at the α/β interface does not exist. Due to the presence of slow diffusing elements like Mo, the time required to achieve equilibrium partitioning is quite long. This can be understood as follows: For small isothermal annealing times, total free energy of the system would be reduced if formation of α takes place, even if it is not formed with the equilibrium composition. Although the reduction in free energy of the system would be lower than if transformation occurs according to equilibrium composition, this is not allowed for by the slow diffusion of alloying elements. As the transformation progresses, the solute elements diffuse towards equilibrium concentrations. Due to the complex composition of the alloy, quantitative validation of this is very difficult. The equilibrium calculations from Thermocalc are not correct, although experiments on isothermal annealing treatments only at 780 °C and 735 °C, for long annealing times, could be carried out.

4.5 ω phase and martensite
For the case of the α or α + β alloys, quenching of the high temperature β phase results in a stabilized β structure having dispersed ω particles and/or martensite phase. The criterion for formation of martensite in titanium alloys uses the concept of so called ‘molybdenum equivalent concept (X_{Mo}).’ This concept employs the molybdenum content as a reference for assessing the influence of other elements on the stability of the β phase. A β alloy becomes metastable at X_{Mo} > 10 wt%. This corresponds to the critical minimum level of β stabilizer content (βC), above which martensite formation is suppressed. This equivalent molybdenum content is given as:
\[ X_{Mo} = 1.0(\%Mo) + 0.67(\%V) + 0.28(\%Nb) + 2.9(\%Fe) + 1.6(\%Cr) + \cdots - 1.0(\%Al) \]

In the present case, the alloy studied, that is, Ti-6.8Mo-4.5Fe-1.5Al, corresponds to \( X_{Mo} = 18.35\% \). Thus, according to the molybdenum equivalent concept, the present alloy under consideration must not form martensite.

The optical micrographs presented in § 4.3.1 with the discussion about influence of solutionizing treatment on the microstructure show a strange kind of behavior. In Figure 4.39, Figure 4.41, Figure 4.43 and Figure 4.47, that is, the samples solutionized at 900 °C for various periods of time, the retained β phase can be seen. It is, however, known that this retained β phase also has dispersed nano-sized ω particles, the presence of which can be detected by using TEM, or by ageing the quenched samples around 300 – 400 °C, where a negative change in length and an increase in hardness indicate the ageing of the ω particles. An example of the negative change in length is shown in Figure 4.78. Further heating till about 600 °C leads to decomposition of the ω precipitates, showing a positive change in length.

![Figure 4.78: Change in length associated with ageing and then decomposition of ω particles. The sample was solutionized at 900 °C for ten minutes, quenched to room temperature, heated again to 900 °C at a rate of 15 °C per minute and quenched to room temperature. The straight lines correspond to rapid heating (once, top line) and quenching (twice).](image)

When Figure 4.42 and Figure 4.45 (samples solutionized at 1050 °C) are inspected, presence of martensite phase inside the retained β phase is confirmed. However, this martensite is seen only for the samples solutionized at 1050 °C, not for the ones solutionized at 900 °C. More examples of martensite are shown in Figure 4.79 and Figure 4.80.
In order to check whether prior partial transformation to $\alpha$ influences the formation of martensite, samples were quenched after solution treatment without annealing. This froze the $\beta$ phase to room temperature and also resulted in $\omega$ particles and/or martensite. The sample solutionized at 900 °C for ten minutes (Figure 4.81) consists of a fully retained $\beta$ microstructure with dispersed $\omega$ particles, confirmed by ageing/decomposition experiment (Figure 4.78). The black particles in the micrograph are inclusions from polishing procedure. The sample solutionized at 1050 °C for one hour (Figure 4.82) consists of retained $\beta$ phase with both martensite phase and dispersed $\omega$ particles. The presence of $\omega$ particles was again confirmed by ageing/decomposition (Figure 4.83).
Figure 4.81: Optical micrograph of sample solutionized at 900 °C for ten minutes and quenched to room temperature.

Figure 4.82: Optical micrograph of sample solutionized at 1050 °C for one hour and quenched to room temperature.
Results and discussion

Two different reasons have been given for this type of dependence of martensite on solutionizing temperature. In Ref. [68], it was said that the non observance of martensite at lower solutionizing temperatures is due to presence of inhomogeneties in the β structure at the solutionizing temperature. In Ref. [69], it was mentioned that lattice softening, occurring at higher solutionizing temperatures, is responsible for the formation of martensite. Thus, according to both these reasoning, having the same β grain size should give rise to the same behavior because diffusion distances and grain growth would be the same. However, this is opposite to what is observed in Figure 4.41, Figure 4.42, Figure 4.43 and Figure 4.45, where same β grain sized samples solutionized at 900 °C do not have any martensite as opposed to the samples solutionized at 1050 °C. Currently, it is not possible to explain the observations.

The comparison of Figure 4.41 and Figure 4.42 shows that even for the same β grain size and same isothermal annealing treatment, the sample solutionized at 900 °C for six hours did not form any martensite, whereas the sample solutionized at 1050 °C for one hour did form martensite. Same is the case for samples solutionized at 900 °C for 36 hours (Figure 4.43, no martensite) and 1050 °C for six hours (Figure 4.45, martensite present). In order to check whether the solutionizing temperature is responsible for formation of martensite, a sample was solutionized at 900 °C for six hours, rapidly heated to 1050 °C in five seconds, held at 1050 °C for 30 seconds and then quenched to room temperature. The microstructure of the heat treatment is shown in Figure 4.84. It can be seen that considerable amount of martensite was formed.
The investigation of martensite formation temperature is very difficult. There is a change in length observed when quenching the samples solutionized at 1050 °C. But, the temperature at which this change in length occurs and the magnitude of the change in length is not reproducible. It was observed that the change in length is generally positive and can occur in the temperature range from 550 °C till as high as 790 °C. In some cases two or even three of these signals were observed. Two examples of this behavior are given in Figure 4.85 and Figure 4.86.
Figure 4.86: Length change signal during martensitic transformation (solutionizing at 1050 °C for one hour and quenched to room temperature).
Chapter 5 Conclusions

The detailed 3-D, orientation and elemental analysis carried out in this project has led to a better understanding of the β to primary α transformation in titanium. The conclusions that can be drawn from the current observations are outlined in this chapter.

It has been shown that three-dimensional analysis is a powerful tool for characterization of microstructures in metal alloys. The analysis of two-dimensional micrographs gives insufficient information, which when extended to 3-D by stereological analysis can lead to generation of incorrect data. For example, approximation of grain shape as ellipsoids, a common method used in stereological analysis, can be unrepresentative of the actual grain shape, more so in the case of branched morphologies.

Nucleation sites of α grains in the material have been identified as β grain corners and β/β grain boundaries for all the regions studied by 3-D analysis. The α particles present inside the β grains are also shown to have originally nucleated at the β/β grain boundaries or β grain corners and then grown inside the β grain. It is a common practice to determine the nucleation density of the α phase from 2-D micrographs, as shown in, for example Figure 4.7, on the basis of the number of α grains per unit area. In view of the connectivity of the α grains following from reconstructions in 3-D space, it is evident that the nucleus densities estimated from 2-D micrographs are too high. For the samples studied by 3-D analysis in the present work it is found that, on average, there are only a few nuclei per β grain, whereas in most cases five to ten times as many branches are observed.

A few growth features of α grains observed are given below:

a) branching of α grains,

b) growth inside one or more β grains,

c) growth along single or multiple β/β grain boundaries,

d) zigzag morphology and bending of β/β grain boundaries and,

e) Widmanstätten needle shaped morphology (a special type of branching).

The mechanism of branching was studied with 3-D orientation analysis. Occurrence of sympathetic nucleation was not observed, a fact deduced from absence of misorientation within the α grains. Interface destabilization, however, could not be validated but some proof in form of optical micrographs was given. One of the most remarkable observations is that planar growth of α grains along β/β grain boundaries or inside the β grains is not sustained. Occurrence of holes inside the α grains was also observed. These characteristics result from 3-D reconstructions, but cannot be identified in 2-D micrographs.

Based on orientation and 3-D information, a mechanism for formation of zigzag morphology in titanium alloys is proposed. Nucleation of an α grain having orientation relationship with β grains on both sides of the grain boundaries and subsequent growth along the β/β grain boundary while maintaining a low energy interface with both the β grains results in the observed morphology. Using data from EBSD, atomic structure of the α/β interface was reconstructed. It was found that the (1100)hcp and (112)bcc planes have a very good matching if placed parallel to the interface. Unlike
the case of FCC-BCC transformations, where the closest packed planes are stacked parallel to the interface, the interface in this case is formed in such a way that the closest packed planes are perpendicular to the interface. This is allowed in a 3-D structure by the ABAB... stacking in both structures (and therefore this orientation relation is essentially different from the FCC-BCC orientation relation) and by the equal distances for the two sets of lattice planes. Zigzag structure is formed due to interfacial constraints during growth whereas branching occurs presumably due to interfacial instability. Study of Widmanstätten morphology indicates various differences from its counterpart in steels. Firstly, there exists no misorientation from start to the tip of the needles. Secondly, at the temperature studied by 3-D analysis, the Widmanstätten needles do not appear in big colonies.

Another important outcome of the orientation analysis is that the so called grain boundary α and the Widmanstätten α growing inside a β grain do not have any α/α grain boundary between them. This makes it important to understand that it is not possible to differentiate between the two types, because both are part of the same crystal.

Not only do the present findings demonstrate that determination of nucleation density from 2-D micrographs should be done with much care, but also that the difference between 3-D reconstructions and 2-D micrographs has major implications for the modeling of phase transformations. The occurrence of intragranular nucleation, spherodization and coalescence are often assumed to take place during the transformation. However, the models incorporating these phenomena are not applicable to describe the nucleation and growth behavior as deduced from the 3-D reconstructions shown in the present work. The present 3-D observations also have serious consequences for the study of variant selection in titanium alloys, since the occurrence of several branches from a single α grain appearing in a 2-D micrograph is of an essential different nature than the occurrence of the same number of separate α grains within the same β grain. The growth of α-Ti from the β phase cannot be described by just plate like growth, but the branching mechanism should be taken into account.

Elemental analysis of the microstructures indicates that the β to α transformation is not diffusion controlled in character. Furthermore, it was shown that the equilibrium calculated using Thermocalc does not hold. Different equilibrium compositions for α and β phases were calculated for two temperatures. It was also observed that solute partitioning between α and β grains increases with increasing isothermal annealing time and the concentrations reached after long annealing times are assumed to be equilibrium values. For short annealing times, local equilibrium across the interface, one of the underlying requirements for diffusion or interface controlled transformations, does not exist. Composition analysis across β/β grain boundaries without transformation shows that there are no compositional inhomogeneities. This means that the reason for no transformation at a few β/β grain boundaries is unrelated to composition but might be due to orientation considerations. Oxygen analysis of a few β grains shows that there might exist a difference between the surface oxygen content of different grains. This can be attributed to orientation dependence of oxide layer thickness, although experimental validation of this fact is difficult for titanium.

Increasing the solutionizing temperature resulted in some interesting observations. Firstly, a higher nucleation density of α grains at the β/β grain boundaries was observed. Secondly, for the same isothermal annealing temperature and time, the equilibrium phase fraction of α was higher than the predicted equilibrium value. This observation might be connected to the results of elemental
analysis in that the equilibrium concentrations and phase fractions as predicted by Thermocalc might not be correct. Thirdly, martensite formation, in an alloy which does not form martensite at lower solutionizing temperatures, was observed. However, it was not possible to understand the mechanisms underlying this behavior.
Chapter 6 Recommendations

Orientation, three-dimensional and elemental analysis were combined in this project to study the β to α transformation. Although a lot of information was obtained, still all the aspects of the transformation are not understood. In this chapter several recommendations are given for further analysis of the transformation, not only with the currently employed characterization methods but also with other techniques.

3-D analysis was carried out only on two heat treatments. This is a major drawback, because, a complete description of the transformation requires analysis of the plate shaped morphologies formed at lower temperatures. However, due to experimental and time limitations, it was not possible to carry out these studies. The other interesting aspect is investigation of dual temperature annealing treatments and continuous cooling treatments. It has been proposed before that if the temperature of the material is suddenly lowered, that is, a dual temperature annealing, the supersaturated amounts of solute elements will provide the driving force for sympathetic nucleation. This aspect of transformation also becomes important for continuous cooling experiments and it is recommended to perform 3-D analysis similar to this work for the heat treatments mentioned previously.

As described in Chapter 5, the currently available models of nucleation and growth of primary α are not applicable for the results presented before. New techniques of modeling need to be employed in order to incorporate branching. The assumption that the transformation is diffusion controlled is also not correct. One way of handling this might be developing a mixed mode model. The complexity of the alloy studied in this project is also a hindrance towards the calculation of equilibrium. The values obtained from Thermocalc are also based on some experiments and extrapolations. It is, thus, very important that the equilibrium values be reevaluated. Although a few attempts towards this were made in the current project, the information is still incomplete, to say the least, and many more experiments at different isothermal annealing temperatures and times need to be done.

Although some proof of non occurrence of sympathetic nucleation is given in this thesis, more experiments need to be done in order to fully understand the phenomenon. It has been shown before, for the case of Widmanstätten in steel, that the α/α grain boundaries are not resolvable by optical microscopy. The EBSD analysis carried out in this project also has a limited accuracy within 1°. Thus, it is recommended that TEM analysis of the microstructures be carried out to (in)validate occurrence of sympathetic nucleation. Furthermore, although interface instability is very well understood for solidification processes, the models for interface instability are not developed enough to include transformation strains, a factor which is very important for the case of solid-solid phase transformations. Investigation of the effect of transformation strains on interface destabilization might make it possible to analyze the basics of interface instability.

It is still not understood why formation of α takes place on some β/β grain boundaries and a few remain completely without nucleation. Extensive studies with EBSD on different heat treatments need to be done in order to calculate the possible effect of type of β/β grain boundary on nucleation of α. However, EBSD alone does not provide full information. Calculation of the parameters of grain boundaries requires 3-D analysis along with orientation information. In this project, even for the EBSD – serial sectioning experiment, orientations in 3-D were not linked. This might prove to be a handy tool for future work. Although, α/β interface reconstruction for the case of zigzag morphology
was carried out on basis of EBSD results, lattice invariant direction could not be analyzed. The combination of TEM analysis is necessary to develop a full description of the interface.

Composition analysis of the plates using WDS was carried out in this project for a few heat treatments. It is recommended that WDS be used for characterization of microstructures formed in order to validate whether extent of partitioning indeed increases with increasing isothermal annealing time. This is also important in lieu of the observation that equilibrium composition of the phases at different temperatures needs to be recalculated using elemental analysis. The study of interstitial elements like O, the detection of which is very complicated, is very important. The orientation dependence of oxide layer thickness should also be investigated. The use of a TEM equipped with EDS analyzer might be more helpful in studying localized distribution of alloying elements, although the special resolution of WDS is better than a normal SEM fitted with an EDS analyzer. This is very important for studying transformation product formed at small isothermal annealing times, when the size of the product phase is too small to be resolved by conventional techniques like WDS.

It is recommended that single solute alloys be investigated in order to try and explain a few of the observations from this project. Although around 70 heat treatments were carried out to try and understand the effect of changing the solutionizing temperature and time, the strange observations listed in Chapter 5 still remain a mystery. It might be an idea to try single solute alloys and carry out similar treatments to investigate the effects like martensite formation, nucleation density, equilibrium fraction of transformation etc. The calculation of equilibrium is much easier in case of alloys having a single alloying element. The crystal structure and type of martensite formed also needs to be studied using XRD. The formation and decomposition behavior of martensite, which could not be understood in this project, needs to be studied in more detail. It might be an idea to combine dilatometry, resistivity and differential scanning calorimetry experiments to investigate this further. Also, quenching of samples to sub-zero temperatures might help in calculating the $M_s$ temperature.
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References


http://picasa.google.com/.


# Appendix A. Heat treatments and microstructures

<table>
<thead>
<tr>
<th>Heat Treatment #</th>
<th>Solutionizing</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>1050 °C for 60 min</td>
<td>615 °C for 10 min.</td>
</tr>
<tr>
<td>20</td>
<td>1050 °C for 60 min</td>
<td>615 °C for 60 min.</td>
</tr>
<tr>
<td>21</td>
<td>1050 °C for 60 min</td>
<td>Continuously cooled to 615 °C in 150 seconds, isothermal annealing at 615 °C for 60 min and continuous cooling to room temperature in 15 min.</td>
</tr>
<tr>
<td>22</td>
<td>1050 °C for 60 min</td>
<td>680 °C for 20 min.</td>
</tr>
<tr>
<td>23</td>
<td>1050 °C for 60 min</td>
<td>680 °C for 120 min.</td>
</tr>
<tr>
<td>24</td>
<td>900 °C for 10 min</td>
<td>720 °C for 6 min.</td>
</tr>
<tr>
<td>25</td>
<td>900 °C for 10 min</td>
<td>720 °C for 120 min.</td>
</tr>
<tr>
<td>26</td>
<td>900 °C for 10 min</td>
<td>720 °C for 1080 min.</td>
</tr>
<tr>
<td>27</td>
<td>900 °C for 10 min</td>
<td>730 °C for 90 min.</td>
</tr>
<tr>
<td>28</td>
<td>850 °C for 120 min</td>
<td>730 °C for 50 min.</td>
</tr>
<tr>
<td>29</td>
<td>900 °C for 1 min</td>
<td>730 °C for 50 min.</td>
</tr>
<tr>
<td>30</td>
<td>900 °C for 10 min</td>
<td>730 °C for 50 min (without vacuum).</td>
</tr>
<tr>
<td>31</td>
<td>900 °C for 10 min</td>
<td>730 °C for 50 min (Helium quenched).</td>
</tr>
<tr>
<td>32</td>
<td>1050 °C for 10 min</td>
<td>730 °C for 50 min.</td>
</tr>
<tr>
<td>33</td>
<td>1050 °C for 60 min</td>
<td>730 °C for 50 min (without vacuum).</td>
</tr>
<tr>
<td>34</td>
<td>1050 °C for 60 min</td>
<td>730 °C for 50 min (initial sample first deoxidized under vacuum at 600 °C for 5000 min and then heat treated).</td>
</tr>
<tr>
<td>35</td>
<td>900 °C for 10 min</td>
<td>730 °C for 50 min, quenching to 680 °C and isothermal annealing at 680 °C for 20 min.</td>
</tr>
<tr>
<td>36</td>
<td>900 °C for 10 min</td>
<td>730 °C for 50 min, continuous cooling to 680 °C in 150 min and isothermal annealing at 680 °C for 20 min.</td>
</tr>
<tr>
<td>37</td>
<td>900 °C for 10 min</td>
<td>760 °C for 10 min.</td>
</tr>
<tr>
<td>38</td>
<td>900 °C for 10 min</td>
<td>760 °C for 15 min.</td>
</tr>
<tr>
<td>39</td>
<td>900 °C for 10 min</td>
<td>760 °C for 30 min.</td>
</tr>
<tr>
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</tr>
<tr>
<td>41</td>
<td>900 °C for 10 min</td>
<td>760 °C for 90 min.</td>
</tr>
<tr>
<td>42</td>
<td>900 °C for 10 min</td>
<td>760 °C for 300 min.</td>
</tr>
<tr>
<td>43</td>
<td>1050 °C for 10 min</td>
<td>760 °C for 90 min.</td>
</tr>
<tr>
<td>44</td>
<td>1050 °C for 60 min</td>
<td>760 °C for 90 min.</td>
</tr>
<tr>
<td>45</td>
<td>1050 °C for 60 min</td>
<td>760 °C for 300 min.</td>
</tr>
<tr>
<td>46</td>
<td>1050 °C for 60 min</td>
<td>760 °C for 600 min.</td>
</tr>
<tr>
<td>47</td>
<td>1050 °C for 60 min</td>
<td>Quenched to room temperature after solutionizing, rapid heating to 760 °C and isothermal annealing at 760 °C for 600 min.</td>
</tr>
<tr>
<td>48</td>
<td>1050 °C for 60 min</td>
<td>760 °C for 1080 min.</td>
</tr>
<tr>
<td>49</td>
<td>1050 °C for 60 min</td>
<td>760 °C for 4080 min.</td>
</tr>
<tr>
<td>50</td>
<td>900 °C for 10 min</td>
<td>790 °C for 1200 min.</td>
</tr>
<tr>
<td>51</td>
<td>1050 °C for 60 min</td>
<td>No isothermal annealing, but isothermal treatment at 900 °C for 60 min and quench to room temperature.</td>
</tr>
</tbody>
</table>

*Quenching from solutionizing temperature to annealing temperature in two seconds.*
Primary α formation at the edge due to high oxygen content
$\alpha$ formation at the edge
Appendix B. EBSD Scans
Color legend for all IPF maps is given below. IPF and phase maps for each scan are given in this appendix. The grain boundaries between α and β grains having Burgers' Orientation Relationship are shown in all the IPF maps in black color. These grain boundaries were created using 'Axis-Angle' criterion, details of which are given in the color legend below. The regions green in color in the phase maps have bcc crystal structure and the regions red in color have hcp crystal structure.

Gray Scale Map Type: <none>

Color Coded Map Type: Inverse Pole Figure [001]
Titanium (Alpha)

Titanium (Beta)

Boundaries: Axis Angle

<table>
<thead>
<tr>
<th>Plane Normal</th>
<th>Direction</th>
<th>Angle</th>
<th>Tolerance</th>
<th>Phase</th>
<th>Match Plane</th>
<th>Fraction</th>
<th>Number</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 1 3</td>
<td>26 1 3</td>
<td>43.5°</td>
<td>5°</td>
<td>Titanium (Beta)</td>
<td>0 0 0</td>
<td>0.340</td>
<td>7969</td>
<td>2.99 mm</td>
</tr>
</tbody>
</table>

*For statistics - any point pair with misorientation exceeding 2° is considered a boundary
(total number = 23468, total length = 8.81 mm)
Appendix B. EBSD Scans

Scan I-1

IPF Map

Phase Map
Scan III-3
Scan III-5
Scan III-8
Scan III-10
Appendix B. EBSD Scans

Scan III-14
Scan III-15
Scan III-16
Scan III-17
Appendix B. EBSD Scans

Scan III-20
Scan III-21
Scan III-23
Scan III-24

[Image of EBSD scan]
Scan III-25
Appendix B. EBSD Scans

Scan III-26
Scan III-29
Scan III-30
Scan III-31
Scan III-32
Appendix B. EBSD Scans

Scan IV-2
Scan V-1
Appendix B. EBSD Scans

Scan VI-1
Appendix C. Additional 3-D structures

Branching along the $\beta/\beta$ grain boundaries and inside the $\beta$ grain

Branching along the $\beta/\beta$ grain boundary
Zigzag morphology