

**MICROSTRUCTURE AND TENSILE PERFORMANCE EVOLUTION DURING
TITANIUM - 6 ALUMINIUM - 4 VANADIUM (Ti-6Al-4V) TEMPORARY HYDROGEN
TREATMENT**

VELILE VILANE



**A thesis presented to the Faculty of Engineering and the Built Environment,
Department of Mechanical Engineering in fulfilment of the requirements for
the conferment of the degree of Doctor of Philosophy in Materials Engineering**

October 2018

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Name: Velile V.N.T. Vilane

Student number: VLNVEL002

Signed by candidate

Signature:

Date: 30/10/18

ACKNOWLEDGEMENTS

When I started my PhD journey I had no clue what I was getting myself into. I also had no idea how I would solve the problems that were presented by the PhD study. So I started from a blank page and blindly searched for solutions. This involved a lot of trial and error, failure and more failure. Eventually I mastered failing and started failing forward, and the latter layered the foundation of my growth as a researcher. The PhD journey was a life-changing experience and it is one of the most fulfilling journeys I have taken.

Without the academic nurturing from my supervisor Professor Robert Douglas Knutsen this project would not have come to completion. I always left supervision meetings with fundamental questions, tackling those fundamental questions slowly unravelled the pieces of the puzzle. Doing a PhD as an international student in South Africa also meant that I had to navigate immigration barriers, this often meant that my direct sources of financial support were limited. Without the grant related financial support from Professor Robert Douglas Knutsen I would not have been able to complete this study. I would also like to acknowledge the National Research Foundation (NRF) and the Department of Science and Technology through their Titanium Centre of Competence (TiCoC) initiative for providing the grant funds that supported me through this study.

Tackling the fundamental questions also meant that I needed to perform high resolution materials characterisation. This was done through research visits to the Centre for High Resolution Transmission Electron Microscopy (CHRTEM) at Nelson Mandela University (NMU). When I started my research visits to CHRTEM I had limited experience with transmission electron microscopy (TEM). Therefore I was very insecure about how I was going to navigate TEM data collection and analysis. I am deeply grateful to my co-supervisor Dr Johan Ewald Westraadt for giving me comprehensive training on transmission electron microscopy and developing my competence as a TEM operator and skilled TEM scientist. I would also like to express my sincere gratitude to the staff and students at CHRTEM who encouraged me and always welcomed me to do science in a safe, inclusive environment.

The Centre for Materials Engineering (CME) has been an academic home. I am privileged to have been a PhD candidate in this centre which not only prioritises academic excellence but also demonstrates extensive human values. The CME team of staff and students provided a safe space that enabled me to express my own vulnerability when I needed to. Having spent more than 70% of my PhD duration in the CME laboratory, I developed a healthy appreciation for the in-house kitchen facility and the coffee supplies. I would also like to thank the CME staff for continually maintaining the kitchen facility and its supplies at no cost to students.

I am grateful to Professor Hamish Fraser and colleagues at the Center for Electron Microscopy and Analysis (CEMAS) for housing me and granting me a valuable research visit to the Ohio State University. I am also grateful to Professor Trevor Sewell and colleagues for granting me overnight access to the Aaron Klug Centre for Imaging and Analysis (UCT CIA). The privilege and convenience that comes with having 24 hour access to highly valued microscopy instruments has been a key contributor to my personal development as an operator.

University of Cape Town (UCT) libraries and the librarians; Dianne Steele, Nuroo Davids and Amina Adam for their prompt responses to my book and journal requests which had to be sourced from an overseas depository.

My friends who taught me about life, love and more importantly taught me about myself; Kealeboga Ramaru, Busisiwe Deyi, Dr Mpati Ramatsoku, Phindile Sabela-Rikhotso. A special thank you to Associate Professor Zethu Matebeni for the life outside of the PhD. Thank you for the love, encouragement, support, the great source of inspiration and supporting me throughout this whole experience, the academic advice, and for always insisting on the draft chapters in moments when I had very little clarity on how I would put all of them together.

My love for academics was very apparent at a very young age, this means that my family has had to put up with me and my academics for as long as I have existed. To my family; Mr Nicholas Vilane, Mrs Elizabeth Vilane, Dumile Nhlengetfwa, Mduduzi Vilane, Mfanelo Vilane, thank you for your patience and for allowing me the space to fully pursue who I am and what I am meant to bring.

DEDICATION

To my beloved parents

Mr Nicholas S. & Mrs Elizabeth Z. Vilane

Thank you for your material, emotional and spiritual support,

Thank you for your unwavering love, which freed me to follow my intuition,

Thank you for your complete acceptance of who I am and what I am meant to bring.

Vilane

Khota,

Mkhulandle,

Wena masisa libalele njengenkhosi!

Wena mbevandvuna!

Wena sitsebe lesihle sekudlela inyama lemanukunuku!

ABSTRACT

This thesis uses temporary hydrogen treatment to refine the cast Ti-6Al-4V microstructure in order to optimise its mechanical properties. It investigates the influence of hydrogen on microstructure evolution, grain refinement and tensile performance. It exposes the unarticulated relationship between hydrogen and titanium aluminide (Ti_3Al) as a gap in literature that has been sustained by the pervasive use of the repeated nucleation framework. It hypothesises that grain refinement of Ti-6Al-4V by temporary hydrogen alloying can cause embrittling effects which remain even when hydrogen is fully expelled from the alloy. It also hypothesises that the hydrogenation-disproportionation-desorption-recombination (HDDR) framework can account for the evolution of grain refinement in hydrogen treated Ti-6Al-4V. This thesis demonstrates that HDDR accounts for microstructure evolution in hydrogen treated Ti-6Al-4V and unveils the intimate relationship between hydrogen and Ti_3Al .

Cast Ti-6Al-4V was refined using hydrogenation-dehydrogenation (HDH), thermohydrogen processing (THP) and thermohydrogen and deformation processing (THDP). Cast Ti-6Al-4V was hydrogenated to 20 at.%H and subsequently dehydrogenated at 675°C (HDH 675), 700°C (HDH 700), 725°C (HDH 725) and 750°C (HDH 750). Hydrogenated Ti-6Al-4V was solution treated (at 900°C), aged (at 580°C) and dehydrogenated (at 675°C or 750°C) during THP treatment. The THDP treatment had a similar processing protocol to the latter, but it incorporated hot deformation (to 1.6 true strain), recrystallisation (at 900°C) and quenching before aging. Microstructure evolution was characterised by X-ray diffraction, electron backscatter diffraction, transmission Kikuchi diffraction and transmission electron microscopy.

Temporary hydrogen treatment causes submicron grain refinement. It improves the yield, tensile strength by up to 70 MPa, 100 MPa (in HDH) or 130 MPa, 142 MPa (in THP) treated Ti-6Al-4V. Hydrogen precipitates Ti-H and Ti-H₂ hydrides which partition Al from its Ti-Al couple. This forms Al rich clusters in neighbouring regions where the degree of Al enrichment stabilises Ti_3Al precipitates. Dehydrogenating at 675°C decomposes hydrides but it retains the Ti_3Al precipitates which deteriorate tensile ductility by up to 75% (in HDH treated microstructures). Dehydrogenating at 750°C significantly dissolves Ti_3Al to extents that retain full ductility (in HDH) and restores 20% ductility (in THP) treated microstructures.

SYMBOLS AND ACRONYMS

at.%	Atomic percent
$\epsilon/\gamma/\delta$	Epsilon (Ti-H)/gamma/delta (Ti-H ₂) – hydrides
α	Alpha phase
β	Beta phase
ASTM	American Society for Testing and Materials
APT	Atomic probe tomography
BCC	Body centred cubic
EBSD	Electron backscatter diffraction
EDS	Energy dispersive spectroscopy
FCC	Face centered cubic
FCT	Face centered tetragonal
FFT	Fast Fourier transforms
FIB-SEM	Focused ion beam SEM
HAADF STEM	High angle annular dark field STEM
HAGB	Higher angle grain boundaries
HCP	Hexagonal close packed
HDH	Hydrogenation-dehydrogenation
HDDR	Hydrogenation-disproportionation-desorption-recombination
HPN	Hydrogen phase naklep
HRTEM	High resolution transmission electron microscopy
IUPAC	International union of pure and applied chemistry
OM	Optical microscopy

PTMC	Phenomenological theory of martensite crystallography
SAD	Selected area diffraction
SEM	Scanning electron microscope
SEM-BSE	Scanning electron microscope - backscattered electron analysis
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscope
THDP	Thermohydrogen and deformation processing
THP	Thermohydrogen processing
THP-BD	Thermohydrogen processing promoting beta decomposition
THP-MD	Thermohydrogen processing promoting metastable phase decomposition
THT	Temporary hydrogen treatment
Ti ₃ Al/ α_2	Titanium aluminide
Ti-6Al-4VxH	Hydrogenated Ti-6Al-4V
TKD	Transmission Kikuchi diffraction
XRD	X-ray diffraction

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CHAPTER 1: INTRODUCTION

1.1 Subject of thesis

Wrought Ti-6Al-4V is the workhorse of the titanium alloy series because it offers an attractive combination of mechanical properties. Its components are traditionally manufactured by machining from wrought stock. Machining is time consuming, has high material waste which escalate the production costs of Ti-6Al-4V components. The high production costs limit the use of Ti-6Al-4V alloys to high end applications like aircraft engine and airframe components.

Casting is an alternative manufacturing route which produces near net shape Ti-6Al-4V components that require minimal machining and this limits the production costs. During casting, molten Ti-6Al-4V is poured into a mould and allowed to slow cool to room temperature. There are ongoing initiatives which incorporate titanium castings into aircraft engines.¹ For example **Figure 1.1** shows a LEAP aircraft engine which is part of a series that incorporates cast titanium components.² These high end applications require cast Ti-6Al-4V components to meet specific performance requirements. However, as-cast Ti-6Al-4V components typically have inferior mechanical properties because of their very coarse as-cast microstructure. They typically require post processing heat treatments to optimise their mechanical properties to meet industry specifications.



Figure 1. 1: The CFM International LEAP aircraft engine which incorporates titanium castings.²

1.2 Background of the thesis

Whilst casting is a cheaper alternative manufacturing route, cast components do not have the best combination of mechanical properties because of their as-cast microstructure. The as-cast microstructure forms from the Widmanstätten growth that occurs when slow cooling Ti-6Al-4V past the beta transus temperature (1050°C). The coarse prior beta grain sizes and the Widmanstätten morphology deter the strength and ductility of cast Ti-6Al-4V components. **Section 1.2.1** elaborates on the Widmanstätten growth that forms the as-cast Ti-6Al-4V microstructure.

1.2.1 Evolution of the as-cast Ti-6Al-4V Widmanstätten microstructure

Figure 1.2 is a montage of optical micrographs of the as-cast Ti-6Al-4V microstructure. As-cast Ti-6Al-4V has a network of coarse prior beta grains with an average prior beta grain diameter of 2000 μm . It also has Widmanstätten (A) and/ or basketweave (B) morphologies.

Figure 1.3 a-d) is a schematic diagram showing as-cast Ti-6Al-4V microstructure evolution during casting. During casting, molten Ti-6Al-4V is cooled below its solidus temperature and its beta transus temperature. At the beta transus temperature, the high temperature allotrope beta phase (β) transforms to the low temperature allotrope alpha phase (α). The beta phase has a body centred cubic (BCC) crystal structure whilst the alpha phase has a hexagonal close packed (HCP) crystal structure.

The BCC to HCP transformation initially occurs at high energy points, therefore alpha phase nucleates at prior beta grain boundaries forming grain boundary alpha as shown in **Figure 1.3 b)**. The nucleated alpha grows into the prior beta grain at a specific orientation that is determined by the BCC/HCP Burgers relationship as shown in **Figure 1.3 c)**. Re-nucleation of alpha occurs when it becomes more energy efficient to nucleate new alpha lamellae than grow the existing lamellae. The basketweave morphology results from re-nucleation of selected HCP alpha variants in the beta phase.



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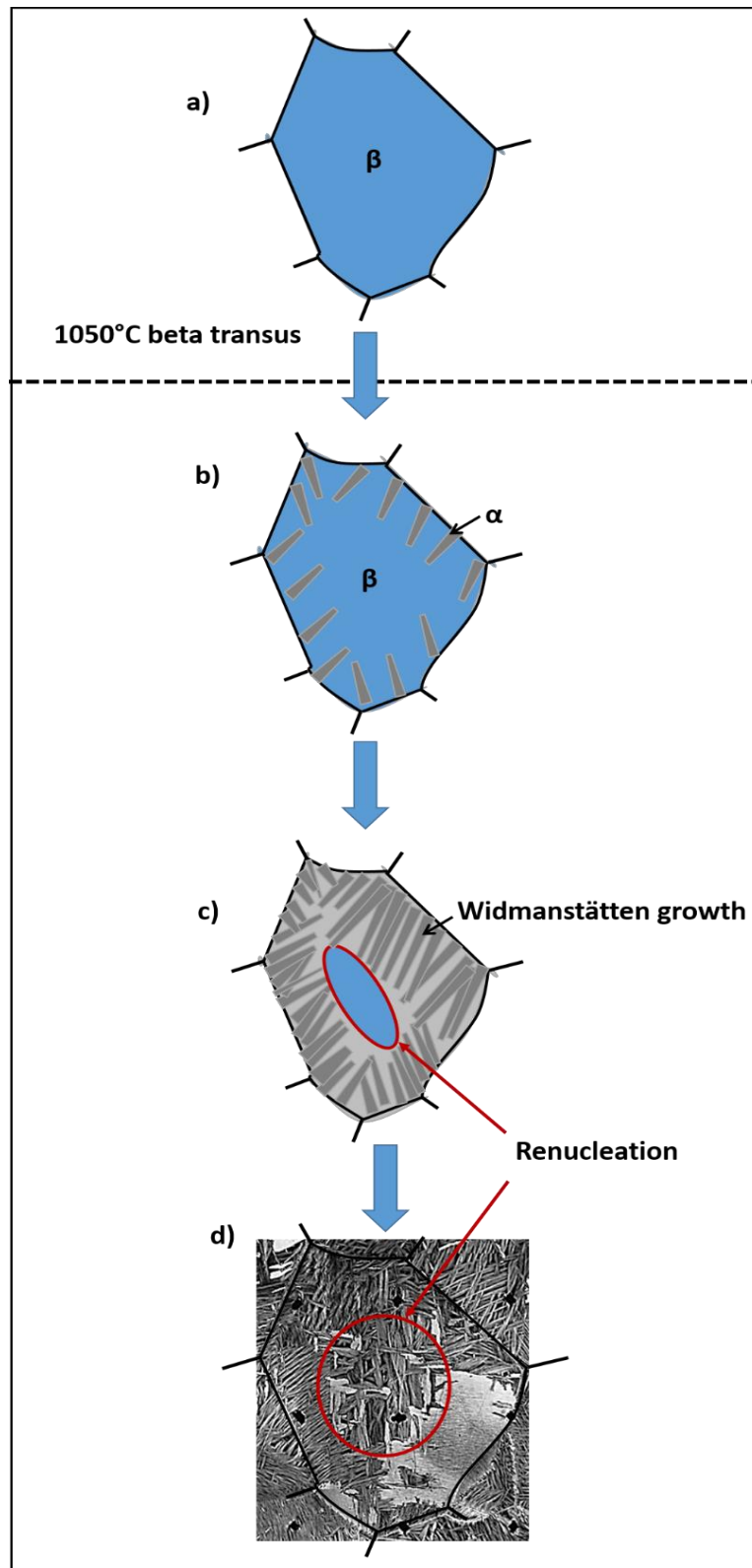


Figure 1. 3: Microstructure evolution of as-cast Ti-6Al-4V during casting showing a) single phase beta region b) nucleation of alpha variants c) and Widmanstätten growth of alpha variants. Image c) also shows the re-nucleation of alpha variants that occurs when it becomes energy efficient to nucleate new variants than grow existing ones. Image d) is the ambient temperature, as-cast Ti-6Al-4V microstructure showing a coarse grained structure, Widmanstätten and basketweave morphologies.

1.2.2 Grain refinement of as-cast Ti-6Al-4V using hydrogen treatment

The coarse prior beta grain sizes and the Widmanstätten morphology reduce the strength and ductility of as-cast components respectively. The grain size and the morphology of as-cast Ti-6Al-4V needs to be refined to optimise the performance of cast components to meet industry specifications.

In a preceding study, ⁴ extensive as-cast Ti-6Al-4V microstructure refinement was achieved after temporary hydrogen treatment. The latter (temporary hydrogen treatment) encompasses heat treatment procedures that are performed on hydrogenated Ti-6Al-4V. The heat treatment procedures promote hydrogen induced phase transformations which refine the microstructure. The alloyed hydrogen is subsequently removed (or dehydrogenated) from hydrogen treated Ti-6Al-4V to avoid hydrogen embrittlement. The preceding study successfully refined as-cast Ti-6Al-4V grain size diameters from 2000 μ m (2mm) to submicron level (less than 1 μ m), and significantly modified the Widmanstätten morphology using temporary hydrogen treatment. ⁴

The Hall–Petch equation describes the relationship between grain size and yield strength, and naturally fine grain sizes yield high strength at ambient temperatures. In the same light, titanium literature has demonstrated that finer lamellae and colony sizes improve the tensile performance of lamellar microstructures. ⁵⁻⁷ For these reasons, a submicron grained microstructure is expected to yield high strength performance. However, this is not automatically true in hydrogen treated Ti-6Al-4V because of the seemingly unexpected embrittlement that can arise even after hydrogen is expelled from the alloy.

1.3 Problem statement

It is hardly known that (outside of hydrogen embrittlement which is eliminated by dehydrogenation) there are additional microstructure embrittling effects that are caused by temporary hydrogen treatment. The additional effects remain in the microstructure after dehydrogenation. This is because Ti-6Al-4V temporary hydrogen treatment not only causes grain refinement, but it also promotes (Ti₃Al) precipitation. The Ti₃Al precipitate is a brittle

intermetallic phase which deteriorates the room temperature tensile performance of hydrogen treated Ti-6Al-4V.

This problem is perpetuated by the fact that the room temperature tensile performance of hydrogen treated Ti-6Al-4V is rarely evaluated and reported in open literature. Rare instances occur where the latter is evaluated after full Ti_3Al dissolution.⁸ The elevated temperature tensile performance of hydrogen treated Ti-6Al-4V is occasionally reported. This could be because Ti_3Al embrittlement is less apparent at elevated temperatures.⁹⁻¹² Consequently, grain refinement by temporary hydrogen treatment studies have not investigated the relationship between hydrogen and Ti_3Al , and the consequent effect of Ti_3Al on room temperature tensile ductility.⁸⁻¹²

1.3.1 Why the problem needs to be solved and approach to solution

This problem threatens the improved property benefits that are expected from Ti-6Al-4V hydrogen refined microstructures. It must be addressed because it dampens the efforts that have been invested in developing hydrogen treatments that refine Ti-6Al-4V microstructures. Solving the problem will require an in-depth understanding of the intimate relationship between hydrogen and Ti_3Al . This thesis takes a bottom-up approach to solving the problem. It characterises the intimate relationship between hydrogen and Ti_3Al up to atomic resolution. It utilises insights gained from the latter to custom design hydrogen treatments that optimise the room temperature tensile performance of hydrogen treated Ti-6Al-4V microstructures.

1.4 Objectives of thesis

The key objectives of this study are:

- To use hydrogen to promote microstructure refinement, optimise tensile performance but avoid the concomitant Ti_3Al embrittlement.
- To thoroughly investigate the influence of hydrogen on Ti-6Al-4V microstructure evolution in order to uncover the intimate relationship between hydrogen and Ti_3Al .
- To propose a microstructure evolution framework for hydrogen treated Ti-6Al-4V that accounts for the evolution of grain refinement and centralises the intimate relationship between hydrogen and Ti_3Al .

1.5 Hypotheses

This study hypothesises that;

- Grain refinement of Ti-6Al-4V by temporary hydrogen alloying can cause embrittling effects which remain even after hydrogen has been fully expelled from the alloy.
- The hydrogenation-disproportionation-desorption-recombination (HDDR) framework can account for the evolution of grain refinement and explain the promotion of Ti_3Al formation in hydrogen treated Ti-6Al-4V.

The HDDR framework is chosen because it holistically accounts for hydrogen promoted microstructure evolution in Nd-Fe-B alloys.^{13, 14} This holistic approach can address the overarching question on the intimate relationship between hydrogen and Ti_3Al in the Ti-6Al-4V context. However, HDDR has not been microstructurally validated in the Ti-6Al-4V context and this thesis aims to examine whether HDDR could account for microstructure evolution in hydrogen treated Ti-6Al-4V. It will examine the latter in three different temporary hydrogen treatments;

1. Hydrogenation-dehydrogenation (HDH)
2. Thermohydrogen processing (THP)
3. Thermohydrogen and deformation processing (THDP)

1.6 Research questions

The study will address the following research questions when characterising microstructure evolution in the above heat treatments:

1. To what extent does the hydrogenated microstructure reflect disproportionation?
2. To what extent does the desorbed (dehydrogenated) microstructure reflect recombination?
3. What is the effect of desorption (dehydrogenation) temperature on microstructure recombination and the room temperature tensile performance?
4. What is the influence of hydrogen tempering on martensite evolution and the tensile performance of THP treated Ti-6Al-4V?
5. What is the influence of hydrogen tempering on martensite evolution and the degree of grain refinement in THDP treated Ti-6Al-4V?

1.7 Scope of the thesis

The thesis simulates the coarse grain size and the Widmanstätten morphology of as-cast Ti-6Al-4V. It converts wrought Ti-6Al-4V to simulated cast Ti-6Al-4V by vacuum annealing above the beta transus temperature (at 1100°C) and slow cooling to room temperature. This is done to grow the grain sizes (to diameter 2mm) and form the Widmanstätten morphology. The as-cast Ti-6Al-4V microstructure was simulated to avoid the inhomogeneity and porosity defects that are associated with castings.

Simulated cast Ti-6Al-4V is then hydrogen treated to refine the microstructure, improve mechanical performance and investigate the influence of hydrogen on microstructure evolution. Mechanical performance is evaluated by testing tensile rods that are configured to the American society for testing and materials (ASTM) E8 / E8M - 16a standard.

The influence of hydrogen on microstructure evolution is investigated by tracing phase constitution and composition using X-ray diffraction (XRD), electron backscatter diffraction (EBSD), transmission Kikuchi diffraction (TKD) and energy dispersive spectroscopy (EDS). Selected area diffraction (SAD) is used to distinguish the HCP crystal structure of Ti₃Al from that of HCP alpha. The thesis also uses high angular annular dark field (HAADF) scanning transmission electron microscopy (STEM) up to atomic resolution to characterise the influence of hydrogen.

1.8 Plan of development

Chapter 2 reviews the series of events that caused the gap in literature. It highlights the literature gap as the unarticulated relationship between hydrogen treatment and Ti₃Al. It exposes how the limitations of the prominently used microstructure evolution framework (the repeated nucleation framework) sustain the Ti₃Al gap. It subsequently proposes a different framework (hydrogenation-disproportionation-desorption-recombination or HDDR) which has been used to holistically characterise hydrogen promoted microstructure evolution in Nd-Fe-B alloys. However HDDR has not been microstructurally validated in the Ti-6Al-4V context and therefore it informs the hypothesis and research questions of the current study.

Chapter 3 designs three hydrogen treatments to address the research questions developed in **Chapter 2**. The hydrogen treatments are: hydrogenation-dehydrogenation (HDH), thermohydrogen processing promoting metastable phase decomposition (THP-MD) and thermohydrogen and deformation processing (THDP). It also introduces the techniques that were used to characterise microstructure evolution in hydrogen treated Ti-6Al-4V.

Chapter 4 uncovers the intimate relationship between hydrogen and Ti_3Al by investigating the effect of hydrides on elemental partitioning in 20 at.% hydrogenated Ti-6Al-4V. It discusses the elements of hydrogenation-disproportionation that are observed in hydrogenated Ti-6Al-4V. It then proposes a hydrogenation-disproportionation half reaction that explains the evolution of grain refinement and the promotion of Ti_3Al precipitation in hydrogenated Ti-6Al-4V.

Chapter 5 evaluates the tensile performance of HDH treated Ti-6Al-4V. It highlights the contribution of hydrogen promoted grain refinement to the improved tensile strength of HDH treated Ti-6Al-4V. It also highlights the contribution of hydrogen promoted Ti_3Al precipitates to the loss in tensile ductility. The work in **Chapter 5** manipulates the dehydrogenation temperature to retain the improved strength whilst eliminating the ductility loss that is caused by Ti_3Al precipitates.

Chapter 6 evaluates the tensile performance of THP treated Ti-6Al-4V and highlights the contribution of hydrogen tempering to martensite strength. It details the influence of hydrogen on martensite evolution at transitional stages of the THP treatment up to atomic resolution. It highlights the contribution of hydrogen promoted Ti_3Al precipitates to acicular plate martensite embrittlement. The work in **Chapter 6** manipulates the dehydrogenation temperature to eliminate the contribution of Ti_3Al to acicular plate martensite embrittlement. **Chapter 6** also discusses the elements of hydrogenation-disproportionation that are observed in hydrogen tempered martensite. It then proposes a hydrogenation-disproportionation half reaction that explains the evolution of grain refinement and the promotion of Ti_3Al precipitation in hydrogen tempered martensite.

Chapter 7 characterises the influence of hydrogen tempering on martensite evolution at the transitional stages of the THDP treatment. It articulates the intimate relationship between hydrogen and Ti_3Al at atomic resolution and highlights the extensive grain refinement (from 2000 μm to submicron grain diameters) that is achieved in THDP treated Ti-6Al-4V. **Chapter 7** reiterates the elements of hydrogenation-disproportionation that are observed in hydrogen tempered martensite.

Chapter 8 concludes that the HDDR framework can account for the evolution of grain refinement and explain the promotion of Ti_3Al formation in hydrogen treated Ti-6Al-4V. It outlines instances where hydride induced partitioning promoted Ti_3Al precipitation. It then outlines the relationship between the desorption (dehydrogenation) temperature, the degree of recombination and the tensile performance.

1.9 Original contribution of thesis

This study investigates Ti-6Al-4V hydrogen promoted microstructure evolution using a different perspective (HDDR).

- It exposes the Ti_3Al gap that has been created by the prominent use of the repeated nucleation framework which does not centralise the intimate relationship between hydrogen and Ti_3Al .
- It proposes a different framework (HDDR) which has been used to holistically characterise hydrogen promoted microstructure evolution in Nd-Fe-B alloys.
- However, the HDDR framework had not been microstructurally validated in the Ti-6Al-4V context. This study addresses the latter by providing microstructural evidence supporting the occurrence of HDDR in hydrogen treated Ti-6Al-4V.
- The study contributes to knowledge by offering a holistic microstructure evolution framework which addresses Ti_3Al precipitation in hydrogen treated Ti-6Al-4V.
- Providing discourse on hydrogen promoted Ti_3Al precipitation makes it feasible to custom tailor hydrogen treatments to retain the positive benefits of hydrogen treatment (grain refinement and strength improvement) whilst avoiding the negative effect (Ti_3Al precipitation and ductility loss).

CHAPTER 2: LITERATURE REVIEW

Temporary hydrogen treatment (THT) is a technique that has been used to refine the coarse cast Ti-6Al-4V microstructure in order to improve mechanical properties. During THT, hydrogen is alloyed to Ti-6Al-4V and subsequent heat treatments are performed on hydrogenated Ti-6Al-4V to promote hydrogen induced phase transformations. The alloyed hydrogen is subsequently removed from the microstructure to decompose hydrogen induced phases and prevent hydrogen embrittlement.

2.1 Advantages of using hydrogen for the refinement of coarse cast Ti-6Al-4V

Hydrogen is used for Ti-6Al-4V grain refinement because it induces phases (hydrogen induced phases) that promote grain refinement.

The grain refinement that occurs during temporary hydrogen treatment is attributed to the repeated nucleation that occurs when hydrogen induced phases precipitate and subsequently decompose.^{10, 11, 15-20} For this reason, THT offers a non-destructive option to significantly modify the microstructure and enhance the mechanical property performance of near net shaped Ti-6Al-4V castings.²¹

The use of hydrogen to promote Ti-6Al-4V grain refinement is also viable because hydrogen is a temporary alloying element that can be removed from Ti-6Al-4V after THT treatment. Therefore hydrogen has more attractive benefits when compared to other alloying elements that promote Ti-6Al-4V grain refinement. For instance, boron is a permanent alloying element which also promotes Ti-6Al-4V grain refinement. Its presence in boron modified Ti-6Al-4V has raised questions on the potential detrimental effects that it can induce to the mechanical performance.²² The use of hydrogen is also more attractive because hydrogen treatment achieves a greater degree of refinement (up to submicron grain formation) when compared to boron alloying which only refines Widmanstätten lamellae widths.²²

2.1.1 Types of temporary hydrogen treatments

Various temporary hydrogen treatments are used to refine Ti-6Al-4V microstructures as shown in **Table 2.1**. These techniques generally consist of: a hydrogenation step, a quench or slow cool step from solution temperature, an isothermal anneal step to promote a beta eutectoid or a metastable phase decomposition and a dehydrogenation step to remove hydrogen. However, some of the treatments do not have intermediate processing steps; they simply alloy and subsequently remove hydrogen. In addition, some treatments incorporate deformation to enhance deformability and improve grain refinement.

The various THT treatments can be broadly classified into four categories;

- I. **Hydrogenate - solution treat - quench - anneal - dehydrogenate:**
Thermohydrogen processing promoting metastable phase decomposition (THP-MD)
- II. **Hydrogenate - solution treat - slow cool - anneal - dehydrogenate:**
Thermohydrogen processing promoting beta decomposition (THP-BD)
- III. **Hydrogenate and incorporate deformation:**
Thermohydrogen and deformation processing (THDP)
- IV. **Hydrogenate and subsequently dehydrogenate (no intermediate steps):**
Hydrogenation-dehydrogenation (HDH)

Table 2. 1: Various temporary hydrogen treatments that have been used to refine Ti-6Al-4V microstructures.²¹

Temporary hydrogen treatment	Protocol
Hydrovac (HVC) ^{23, 24}	H - β solution treat - WQ - Age - DH
Constitutional solution treatment (CSC) ²⁵	H in β region - cool below ET - DH
Below β transus hydrogenation ^{20, 26}	H below β transus - cool to RT - DH below β transus
Repeated eutectoid β phase decomposition ²⁷	H above β transus - cool below ET - repeat cycle - DH
Repeated martensitic β phase decomposition ²⁷	H above β transus - WQ - repeat cycle - DH
HHWD 1 ^{28, 29}	H - deform below transus - DH below deformation T
HHWD 2 ^{30, 31}	H - deform above transus - DH below transus

H - hydrogenate; WQ - water quench; DH - dehydrogenate; ET - eutectoid temperature; RT - room temperature; T - temperature

2.2 Evolution of grain refinement by temporary hydrogen treatment

Hydrogen has not always been of positive value in the heat treatment of metals. The focus of hydrogen research in metals evolved from “eliminating hydrogen in metals” (in the 1950s) to “using hydrogen to promote grain refinement” (by the 1970s). This shift in paradigm was the birth of grain refinement by temporary hydrogen alloying. Over time, research efforts were invested in improving the understanding of hydrogen promoted microstructure refinement. As a result, this led to phase diagrams and foundation framework proposals.

2.2.1 The 1950s: hydrogen was only seen as a harmful element in metals

The influence of hydrogen on metals was no stranger to engineers and research scientists in the 1950s. Dissolved hydrogen presented an unpredictable weakening of engineered metallic structures due to hydrogen embrittlement. The history of engineering documents several examples of hydrogen catastrophes: hydrogen corrosion in the petrochemical industry, hydrogen flaking of rails and aircraft crashes due to hydrogen embrittlement.³² Consequently, the only existing paradigm at the time was eliminating hydrogen from metallic structures. Research generated by the scientific community focused on removing hydrogen and any work on the positive effects of hydrogen on metals was unthinkable.

2.2.2 The 1960s: hydrogen induced plasticity was discovered

The 1960s introduced the first positive way of engaging with hydrogen research in metals. Goltsov³² reports that Schleicher and Zwicker pioneered hydrogen induced plasticity in titanium alloys. They (Schleicher and Zwicker) argued that since hydrogen stabilises the more deformable BCC allotrope of titanium at lower temperatures, it could be used to improve the lower temperature deformability of titanium alloys. This line of thought was resisted by scientists because of the heightened sensitivity on the harmful effects of hydrogen that existed at the time. Schleicher and Zwicker's³² ideas were rejected by world class publications which confirmed hydrogen as a harmful element in metals.

2.2.3 The 1970s: hydrogen induced polymorphism was discovered

The discovery of hydrogen induced polymorphism in the 1970s added to the “positive effects of hydrogen” discourse. Hydrogen induced polymorphism was initially introduced as the hydrogen phase naklep (HPN) concept,^{32, 33} whereby metals could be controllably strengthened by promoting hydrogen induced phase transformations. Hydrogen induced polymorphism caused the paradigm shift towards the positive use of hydrogen in metals. The success of hydrogen induced polymorphism was owed to;

- Its versatile strengthening that could be applied in polymorphic and non-polymorphic materials.
- Its non-destructive strengthening that could be achieved without deformation.

2.2.4 The 1970-1990`s: positive hydrogen research emerges

Since research on preventing hydrogen embrittlement had been commissioned in the 1950s, it is most likely that scientists had improved their skills on removing hydrogen from metals by 1970. Therefore scientists had more leeway to explore the concept of hydrogen strengthening because they could subsequently remove it and prevent embrittlement. The attractive benefits of hydrogen processing (versatile, non-destructive strengthening) combined with improved skills on preventing hydrogen embrittlement broke the negative paradigm of conducting hydrogen research in metals. This launched a positive hydrogen research era. By 1995, sufficient data supporting the positive influence of hydrogen in metals had been produced and it was presented at the first international conference on hydrogen treatment of materials.^{34, 35}

The 1970-1990`s were a crucial time in the hydrogen treatment of titanium alloys. During this period, the grain refinement of Ti-6Al-4V by temporary hydrogen treatment was reported (in 1979),³⁶ and half of the available hydrogenated Ti-6Al-4V (Ti-6Al-4VxH) phase diagrams were proposed (**Section 2.3**). More importantly, these phase diagrams affected the Ti-6Al-4VxH foundation frameworks that were formulated at the time. These foundation frameworks are used to predict or interpret microstructure development during hydrogen processing. The extent to which these foundation frameworks comply with what is currently observed in hydrogenated Ti-6Al-4V is the basis of the argument in this work, as presented in **Sections 2.4-2.5**.

2.3 The Ti-6Al-4VxH phase diagrams 1980-2001

Figure 2.1 a-c) shows the Ti-6Al-4VxH phase diagrams that were proposed between 1980 and 2001. Two Ti-6Al-4VxH phase diagrams were initially proposed by Kerr et al.²⁴ and Ilyin et al.³⁷ between 1980 and 1990.

Kerr et al.²⁴ derived the first phase diagram in 1980 and this was closely followed by Ilyin et al.³⁷ in 1992. These authors had similar views on the fact that hydrides precipitate at a minimum hydrogen content of 15 at.%H. However their work had differences on the high temperature stability of hydrides. Kerr et al.²⁴ proposed that hydrides were stable up to 900°C; on the contrary Ilyin et al.³⁷ proposed that hydrides were only stable below 250°C. In 2001, Qazi et al.¹⁶ introduced the third Ti-6Al-4VxH phase diagram. Qazi et al.¹⁶ supported Kerr's ideas on the high temperature stability of hydrides by confirming a dual phase region between 800°C-900°C which consisted of beta and hydride phases.

All the Ti-6Al-4VxH phase diagrams proposed within the period of 1980 to 2001 share a commonality: they only document alpha, beta and hydride phases. Since alpha and beta are equilibrium Ti-6Al-4V phases, the hydrides were the only documented hydrogen induced phase at the time.

In summary Kerr et al.,²⁴ Ilyin et al.³⁷ and Qazi et al.¹⁶ had differing views on hydride phase regions. Their differences were unified by a common view that documented hydrides as the only hydrogen induced phase in the Ti-6Al-4VxH system. Today, this common view has a traceable impact on the grain refinement by temporary hydrogen alloying frameworks that were formulated at this time. The most common foundation framework that was formulated at this time is the repeated nucleation framework.¹⁸ It is currently commonly used to explain evolutionary mechanisms in hydrogen treated microstructures. ^{10, 11, 15-20}

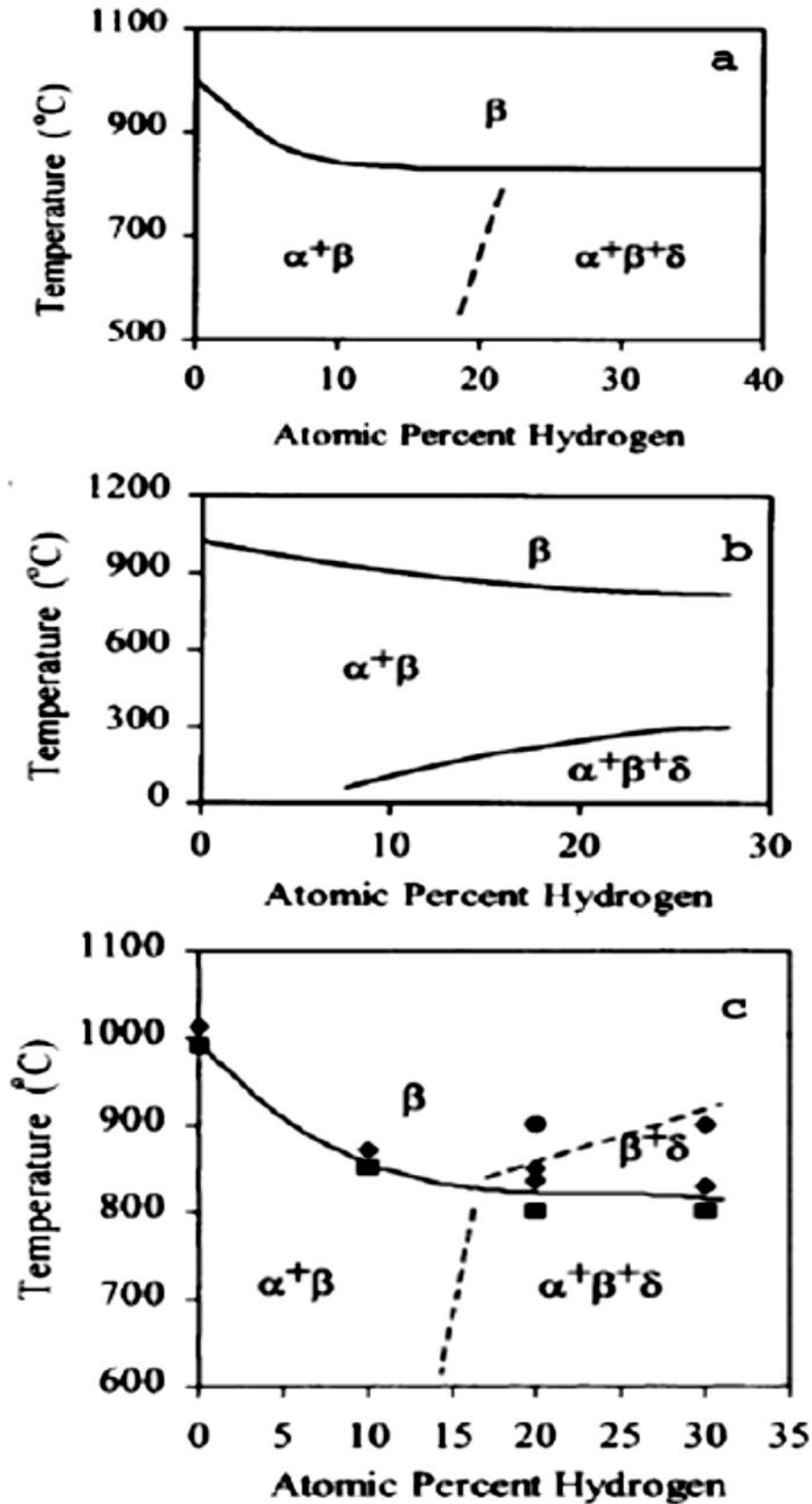


Figure 2. 1: The 1980-2001 Ti-6Al-4VxH phase diagrams proposed by a) Kerr et al.²⁴ b) Ilyin et al.³⁷ c) Qazi et al.¹⁶ The commonality between these phase diagrams is that they only document hydrides (δ) as a hydrogen induced phase.

2.4 The repeated nucleation framework

The repeated nucleation framework is a prominent framework that has been used to explain microstructure evolution during hydrogen treatment.^{10, 11, 15-20} The repeated nucleation framework attributes grain refinement (during hydrogen treatment) to the repeated nucleation and decomposition of the hydride phase. The gist of this framework is outlined in **Equation 1**: during hydrogenation, alpha absorbs hydrogen and transforms to hydrides, which subsequently decompose during dehydrogenation to nucleate equilibrium alpha and beta.

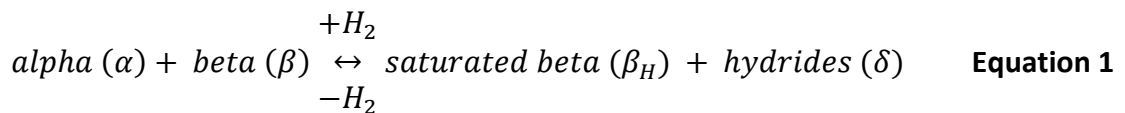


Figure 2.2 a-c) shows schematic diagrams which use the repeated nucleation framework to interpret the evolution of submicron grain refinement during a THDP treatment. It describes a THDP procedure with the sequence of steps: martensite transformation, low temperature deformation (in hydride region) and dehydrogenation (at recrystallisation temperature). Yoshimura's¹⁸ study interpreted that martensite transformation formed martensite plates which subdivided prior beta grains. Subsequent deformation induced a) a dislocation cell network which acted as nucleation points for finely dispersed hydrides. Hydride precipitation had an associated volume expansion which also induced a high density of dislocations in the matrix. Subsequent dehydrogenation b) decomposed the finely dispersed hydrides and c) nucleated submicron grains at the hydride induced dislocations.

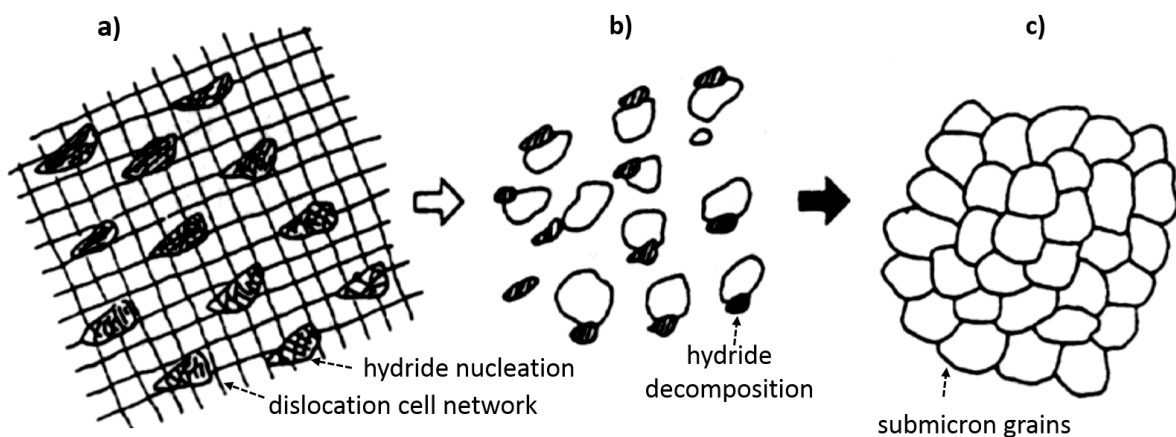


Figure 2. 2: Schematic diagrams which use the repeated nucleation framework to interpret the evolution of grain refinement during a THDP treatment. Image a) shows nucleation of finely dispersed hydride precipitates at a deformation induced dislocation cell network. The nucleated hydrides induce high density dislocations which act as b) nucleation points for c) submicron grains during dehydrogenation.¹⁸

2.4.1 The point of departure: Limitations of the repeated nucleation framework

The repeated nucleation framework¹⁸ associates the grain refinement which occurs during temporary hydrogen treatment to the precipitation and decomposition of a hydrogen induced phase (hydrides). This is primarily indicative of the time when it was formulated (when hydrides were the only documented hydrogen induced phase). However, the scope of this framework becomes limited when considering that some articles report Ti_3Al precipitates in hydrogen treated Ti-6Al-4V. The repeated nucleation framework offers limited background on the phase evolution events that occur during hydrogen treatment. Its scope is limited to hydrides and overlooks Ti_3Al .

2.4.2 Possible reasons why the repeated nucleation framework excludes a Ti_3Al discourse

2.4.2.1 Phase diagram influence

The repeated nucleation framework emphasizes the repeated nucleation and decomposition of the hydride phase. This may be a result of a strong allegiance to the 1980-2001 Ti-6Al-4VxH phase diagrams which only documented hydrides as the only hydrogen induced phase. The phase diagram is a powerful tool that has been used by researchers in formulating foundation frameworks. Since research promotes referencing of supporting ideas, the phase diagram can assert a certain degree of authoritative power which tunes perspectives of research outputs. Allegiance to the 1980-2001 Ti-6Al-4VxH phase diagrams (which exclude the Ti_3Al phase) can promote the ill-consideration or even elimination of undocumented phases like Ti_3Al . If a phase diagram is used as a reference, it is highly likely that its documented phases will be prioritised when formulating foundation frameworks.

2.4.2.2 The inverse optimisation approach to refinement that is observed in grain refinement by temporary hydrogen treatment literature

It is common that grain refinement by temporary hydrogen treatment studies take the inverse optimisation approach to refinement. They focus on achieving the smallest grain sizes possible with less emphasis on the underlying evolutionary events that lead to grain refinement. The inverse optimisation approach uses microstructure investigation as a protocol to confirm check-listed phases, rather than explore microstructure evolution. An

explorative approach would involve the use of complementary techniques to investigate several aspects of the microstructure rather than utilising one tool. The inverse optimisation approach is a biased approach to microstructural study and can result in researchers missing crucial microstructure evolution information.

One classic example of the inverse optimisation approach is observed in Yoshimura et al.^{9, 10, 18, 19} where Ti_3Al precipitates could be missed by only relying on TEM selected area diffraction (SAD) to detect them. In this instance, the size of Ti_3Al precipitates is key in their detection. If Ti_3Al precipitates at nanometre scales in some regions of alpha phase, the size and position of the analysed region is key in their detection.

Therefore, successful Ti_3Al detection requires complementary bulk scale techniques that accommodate the limited sampling of TEM analysis. The use of complementary techniques is not reported in the former Yoshimura et al.^{9, 10, 18, 19} studies because they were approached from an inverse optimisation point of view. Therefore, the absence of Ti_3Al in these studies is questionable.

In summary, a gap in literature exists because the repeated nucleation framework does not address Ti_3Al precipitation in hydrogen treated Ti-6Al-4V. The existence of this gap has been attributed to: influence from the 1980-2001 Ti-6Al-4VxH phase diagrams (which do not document Ti_3Al) and the largely inverse optimisation approach to grain refinement in grain refinement by temporary hydrogen treatment studies.

Consequently, the repeated nucleation framework does not fully exhaust the microstructure evolution events that occur during hydrogen processing. **Section 2.5** discusses the existing gap in literature created from the exclusion of a Ti_3Al discourse by the repeated nucleation framework. In this gap, grain refinement by temporary hydrogen treatment literature inconsistently documents Ti_3Al precipitates; it also does not clarify the intimate relationship between hydrogen and Ti_3Al .

2.5 Gap in literature: The inarticulate relations between hydrogen and Ti_3Al

Identification of Ti_3Al precipitation in hydrogen treated Ti-6Al-4V has been excluded by the prominent focus of THT foundation frameworks on grain refinement. Therefore, the causes of Ti_3Al precipitation in hydrogen treated Ti-6Al-4V are poorly understood because they are not articulated in literature. This inarticulate relationship between hydrogen and Ti_3Al is a gap in literature that manifests in two ways:

- Inconsistencies in Ti_3Al documentation in grain refinement by temporary hydrogen treatment literature.
- Lack of a scholarly investigation on the relationship between hydrogen and Ti_3Al precipitation.

The prevalent inconsistencies of Ti_3Al representation in literature are observed in studies which performed related hydrogen treatments. These related studies do not have a unified voice on Ti_3Al precipitation, some studies report Ti_3Al precipitates whilst others do not. Examples of the Ti_3Al phenomenon are shown in **Table 2.2**.

In **Table 2.2**, a collection of Ti-6Al-4V grain refinement by temporary hydrogen treatment studies has been grouped as related treatments. The term related treatments/studies describes all treatments/studies that can be categorised into either hydrogenation-dehydrogenation (HDH), beta decomposition (THP-BD), metastable phase decomposition (THP-MD) or those which incorporate deformation (THDP). For instance, studies or treatments that alloy and subsequently remove hydrogen are related to HDH, studies that involve martensite tempering are related to metastable phase decomposition (THP-MD) etcetera. In **Table 2.2**:

- **Author and year:** denote the researcher and publication time of the article
- **Treatment:** denotes the type of THP treatment that was performed in the research
- **at.%H:** denotes the alloyed hydrogen (some articles alloy different concentrations of hydrogen, these varied concentrations were separated by a comma)
- **DH temp:** states the dehydrogenation temperature
- **Ti_3Al / after DH:** indicates if the article reports Ti_3Al before / after dehydrogenation respectively
- **Properties/ (A. temp °C):** states the evaluated mechanical properties/ (ambient temperature)
- **Analysis:** states the reported microstructure analysis techniques in the research

2.5.1 An outline of the inconsistent Ti_3Al representation in grain refinement by temporary hydrogen treatment literature

In **Table 2.2**, prevalent inconsistencies in Ti_3Al representation are observed in THP-BD and THDP studies. For example THP-BD authors Zhang and Zhang⁸ and Il'in et al.³⁸ report Ti_3Al precipitates whilst Guitar et al.³⁹, Liu et al.⁴⁰ and Kerr²³ do not. This inconsistency in Ti_3Al representation cannot be attributed to a lower hydrogen concentration in Guitar et al.³⁹ (13, 19 at.%H) and Liu et al.⁴⁰ (20-22 at.%H) because Kerr²³ reported no Ti_3Al precipitates at 40 at.%H. Similarly, these inconsistencies are observed in THDP work that alloyed up to 30 at.%H whereby Yoshimura et al.^{9, 10, 18, 19} reports no Ti_3Al precipitates whilst Ivanov et al.¹² does. All the THP-MD studies in **Table 2.2** do not report Ti_3Al ; however Ti_3Al has been observed in THP-MD work from the current study.

It can be argued that the observed inconsistencies in Ti_3Al representation are caused by the different annealing temperatures that were used in different treatments. This argument however loses its significance when considering that Ti_3Al precipitates have been observed in Ti-6Al-4V hydrogenated to a minimum of 20 at.%H (with no further treatment).⁴¹ The precipitated Ti_3Al is proposed to dissolve after hydrogen is removed at 750°C,^{42, 43} which makes hydrogen the key variable that promotes Ti_3Al precipitation. Whilst temperature variations (below 750°C) would affect the volume fraction of Ti_3Al , the alloys would still retain some Ti_3Al . Therefore, Ti_3Al representation is expected from any grain refinement by temporary hydrogen treatment research that alloys a minimum of 20 at.% H to Ti-6Al-4V.

2.5.2 Possible reasons behind the inconsistent Ti_3Al representation in literature

Looking at the THP-BD work by Kerr,²³ Il'in et al.,³⁸ and Zhang and Zhang⁸ unfolds that history can limit access to advanced instruments. Kerr²³'s work (published in 1985) possibly faced instrument resolution limits that made nanosized Ti_3Al detection difficult. In comparison, the studies in the 1990's (Zhang and Zhang⁸) and early 21st century (Il'in et al.³⁸) possibly had favourable access to improved instruments with better resolution. The other reason could be the use of complementary phase analysis techniques. In **Table 2.2** most studies which detected Ti_3Al used TEM diffraction in conjunction with XRD. Those that relied on TEM diffraction often did not report Ti_3Al precipitates and the problem with solely relying on TEM diffraction has been discussed in **Section 2.4.2.2**.

Table 2. 2: A collection of studies where hydrogen has been used to promote grain refinement and/or understand its mechanisms.

Authors	Year	Treatment	at.% H	DH Temp (°C)	Ti ₃ Al / after DH	Properties/ (A. temp °C)	Analysis
Yoshimura et al. ⁹	1994	THDP, THP-MD, THP-BD	10, 20, 25, 30, 35	700	x / x	HT Tensile (650-950)	SEM
Yoshimura ¹⁸	1997	THDP	16-32	700	x / x	Fatigue	TEM
Yoshimura et al. ¹⁹	1999	THDP	19	700	x / x	RT Tensile	TEM
Yoshimura et al. ^{10, 11}	2002	THDP	21	600, 700	x / x	RT and HT Tensile (650-950)	TEM
Grabovetskaya et al. ⁴⁴	2006	THDP	15	600	x / x	x	TEM, XRD
Ivanov et al. ¹²	2010	THDP	26-30	600	✓ / ✓	HT Tensile (600)	TEM, XRD
Qazi et al. ¹⁵	2003	THP-MD	10, 20, 30	750	x / x	x	TEM, XRD
Qazi et al. ¹⁶	2001	THP-MD	10, 20, 30	750	x / x	x	TEM, XRD
Sun et al. ⁴⁵	2009	THP-MD	17, 27	700	x / x	RT tensile	SEM
Yuan et al. ⁴⁶	2009	HDH	13	750	x / x	RT Tensile	SEM, TEM, XRD
Zhao et al. ⁴⁷	2010	HDH	8, 13, 19	700	x / x	x	XRD, SEM, TEM
Yu et al. ⁴⁸	2006	HDH	41	600	✓ / x	x	TEM, XRD
Shen et al. ⁴³	2009	HDH	34, 41	600, 750	✓ (>20 at.%H) / x	x	TEM, XRD
Shen et al. ⁴⁹	2014	HDH	10, 20, 30, 35, 45	600	✓ (>20 at.%H) / ✓	Hot Compression YS (600)	TEM, XRD
Zhang et al. ⁴¹	1992	H	10, 20, 26	x	✓ (>20 at.%H) / not DH	x	TEM, XRD
Luo et al. ⁵⁰	2006	H	8, 15, 19	x	x / x	x	TEM, XRD
Shan et al. ⁵¹	2007	H	11, 13, 19	x	x / x	x	XRD, SEM, TEM
Tsai and Wang ⁵²	2017	H	10, 23, 35, 38, 43	600	✓ / ✓	x	XRD, SEM, TEM
Liu et al. ⁴⁰	2008	THP-BD	20-22	760	x / x	x	SEM, TEM, XRD
Kerr ²³	1985	THP-BD	19, 24, 30, 40	650, 675, 700, 760	x / x	RT tensile	TEM
Zhang and Zhang ⁸	1997	THP-BD	32	700, 750, 800, 850	✓ / x	RT tensile, RT Fatigue	XRD, TEM
Il'in et al. ³⁸	2008	THP-BD	29	600-650	✓ / ✓	x	TEM
Guitar et al. ³⁹	2009	THP-BD/ THP-MD	13, 19	675, 750	x / x	RT tensile	EDS, SEM, TEM
Sun et al. ⁴²	2015	HDH	up to 50 at.%H	0-900	✓ / x (dissolved at 750)	x	XRD/TGA/DSC

at.%H - amount of dissolved hydrogen; **DH Temp** - dehydrogenation temperature; **Ti₃Al/after DH** - aluminide presence before/ after dehydrogenation; ✓ - present; X - not present; **RT** - room temperature; **HT** - high temperature **Grey** - studies reporting Ti₃Al

2.6 Why this research needs to be undertaken

This research needs to be undertaken to address the gap in literature which can be observed in studies that overlook Ti_3Al precipitation, mention Ti_3Al but offer limited insights on microstructure evolution, propose an evolution mechanism but lack microstructure evidence, or rely on hardness measurements to evaluate mechanical performance. In addition, this research must be performed to contribute to the advances that literature has made towards understanding the contribution of hydrogen to grain refinement and Ti_3Al precipitation.

2.6.1 Information gap in studies which overlook Ti_3Al

The 2015 Ti-6Al-4VxH phase diagram proposes Ti_3Al as a dominant hydrogen induced phase in the Ti-6Al-4VxH system. This implicates the 1980-2001 phase diagrams, the repeated nucleation framework and the Ti-6Al-4VxH studies that overlook Ti_3Al precipitation. **Figure 2.3** shows the recently proposed hydrogenated Ti-6Al-4V (Ti-6Al-4VxH) phase diagram. It highlights the extensively used annealing region in grain refinement by temporary hydrogen treatment studies (500°C - 750°C) by red dotted lines. The solid green line highlights the expected phases at a hydrogen concentration of 20 at.% H.

Observations from **Figure 2.3**:

- At 20 at.%H, Ti_3Al is the predominant hydrogen induced phase; hydrides are only stable at temperatures below 150°C.
- In the extensively used annealing region (500°C-750°C), hydrides are only expected to precipitate at hydrogen concentrations above 42 at.%H.
- Between 15 at.%H and 42 at.%H, samples treated in this region (500°C-750°C) will only have hydride precipitates if they were slow cooled from soaking temperature (not quenched) because slow cooling would allow annealing time in the hydride region.

Slow cooling is performed in beta decomposition studies, and thus hydrides are expected in beta decomposed Ti-6Al-4V. On the contrary, quenching is performed in martensite decomposition studies and according to the 2015 Ti-6Al-4VxH phase diagram hydrides are not expected in martensite that was tempered between 500°C and 750°C (at hydrogen concentrations below 42 at.%H). However, tempered martensite studies report hydrides after tempering 30 at.% hydrogenated Ti-6Al-4V martensite between 500°C and 750°C.¹⁵⁻¹⁷

The latter paragraph illustrates the extent to which hydrogen promoted microstructure evolution mechanisms in Ti-6Al-4V can be misinterpreted from primarily referencing information that is documented in phase diagrams. It also illustrates the role that volume fractions of alpha and beta phases play in hydride precipitation. For instance, beta phase dissolves more hydrogen (up to 42 at.% H)^{43, 51} compared to alpha phase which dissolves up to 8 at.%H.^{8, 43} Therefore, a beta to alpha phase decomposition (in 20 at.% hydrogenated Ti-6Al-4V), can saturate alpha with hydrogen and promote hydride precipitation when annealing between 500°C and 750°C.

In summary, Ti₃Al is expected to precipitate in studies that alloy at least 20 at.%H⁴¹ and subsequently anneal between 500°C and 700°C. However, it is not always reported. Therefore, there is a need for a microstructure focused study to investigate the influence of hydrogen on the evolution of grain refinement and Ti₃Al precipitation in hydrogen treated Ti-6Al-4V.

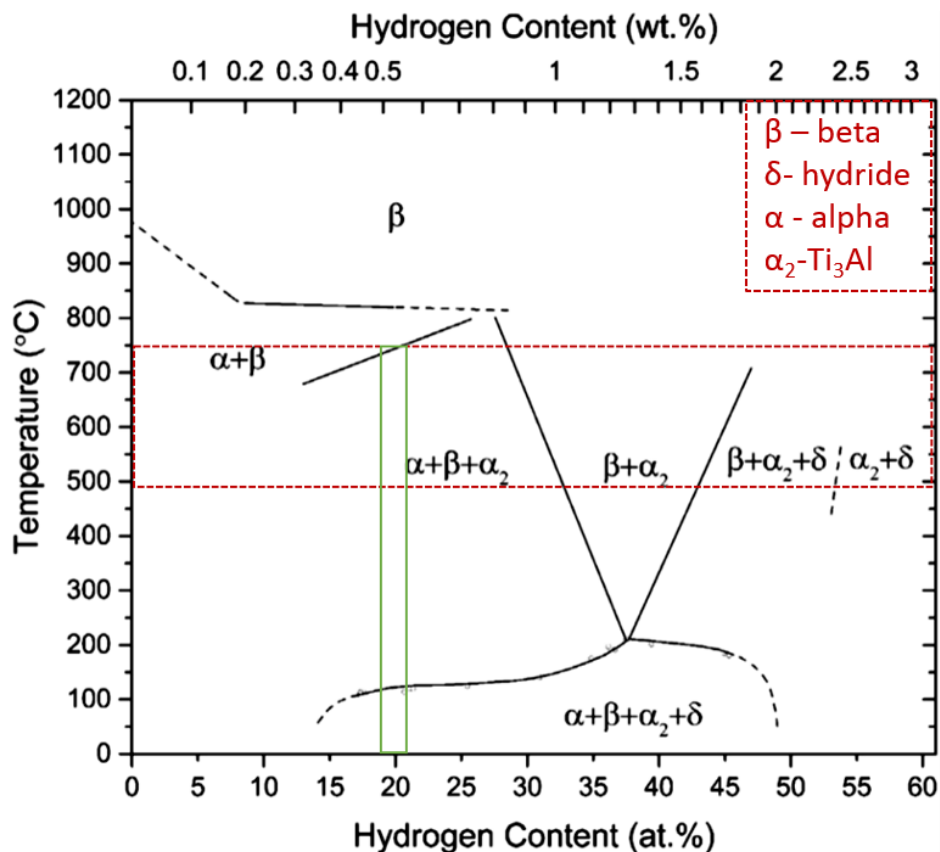


Figure 2. 3: The 2015 Ti-6Al-4VxH phase diagram proposes titanium aluminide (Ti₃Al or α₂) as a stable phase in the Ti-6Al-4VxH system.⁴² The red dotted region highlights the common annealing temperature region used in grain refinement studies. The solid green region demarcates the focus region in this work (because current study alloys 20 at.%H).

2.6.2 Significant advances made towards understanding hydrogen promoted microstructure evolution

This section documents the significant literature contributions that have enhanced the understanding of hydrogen promoted microstructure evolution with respect to grain refinement and Ti_3Al precipitation.

The precipitation of Ti_3Al in hydrogen treated Ti-6Al-4V was initially understood to be a consequence of the beta stabilising effect of hydrogen.^{21, 37, 38} It was attributed to the consequent enrichment of alpha phase with aluminium (Al) that occurred when hydrogen stabilised a greater volume fraction of beta phase at lower annealing temperatures.^{21, 37, 38}

Il'in et al.³⁸ illustrated this understanding in the schematic diagrams in **Figure 2.4 a-d**). The equiaxed Ti-6Al-4V starting microstructure a) had an average Al content of 7 at.%Al and 3 at.%Al in its alpha and beta phases respectively.³⁸ In **Figure 2.4**, hydrogenating in the alpha plus beta region b) increased the volume fraction of BCC phase. Aluminium consequently partitioned from beta towards the decreased volume fraction of alpha. This enriched alpha with Al to concentration levels that stabilised the Ti_3Al phase. Subsequent isothermal anneal at the eutectoid temperature c) promoted a hydrogen saturated beta to alpha and hydride decomposition. The eutectoid products (alpha and hydride) were lean in Al compared to the primary alpha because they nucleated from a parent beta phase that was lean in Al. Dehydrogenating between 600°C and 700°C d) decomposed hydrides to nucleate refined alpha phase. However, this dehydrogenation temperature range did not support sufficient Al diffusion to dissolve the precipitated Ti_3Al . Therefore, the dehydrogenated microstructure consisted of Al lean alpha, Al rich Ti_3Al and beta phase.

This stride outlines some of the evolutionary events which promote Ti_3Al precipitation in hydrogen treated Ti-6Al-4V. However, it does not fully articulate hydrogen promoted microstructure evolution because it does not delve into the likelihood of hydrides precipitating in the Al rich primary alpha phase. It therefore lacks perspective on the effect of hydrides on elemental composition, but it can be enhanced by Rosenberg's observations on the effect of hydride precipitates on Al enrichment within the alpha phase.⁵³

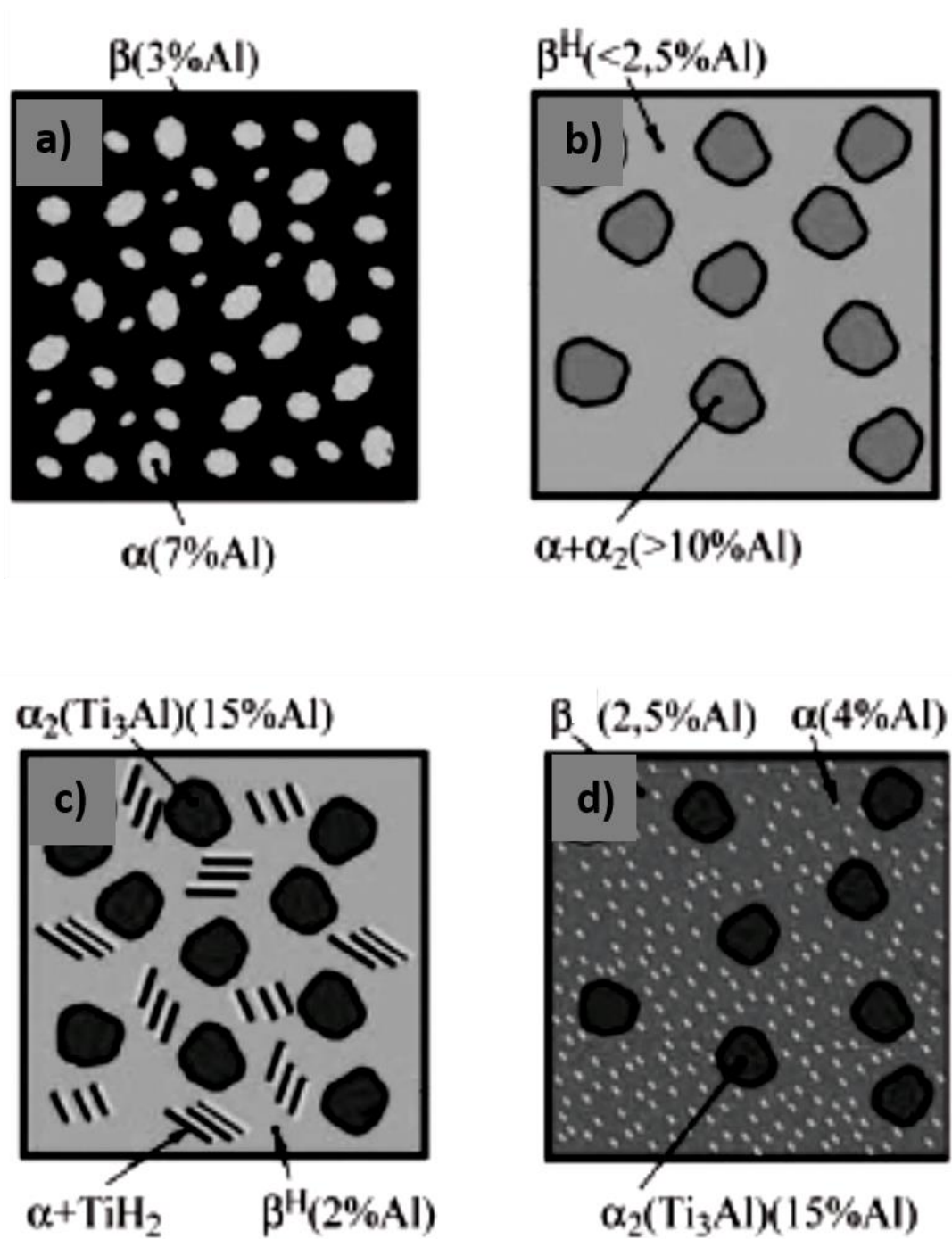


Figure 2. 4: Schematic diagrams showing the evolution of aluminium composition in a) an equiaxed Ti-6Al-4V microstructure through the b) hydrogenation (in alpha plus beta region) c) eutectoid decomposition and d) dehydrogenation (between 600°C and 700°C) stages of a temporary hydrogen treatment. ³⁸

Rosenberg⁵³ alluded to Ti_3Al precipitation in hydrogen treated Ti-6Al-4V being explained by the fact that hydride precipitation increased the Al concentration in the alpha phase. This effect (hydrides promoting the enrichment of alpha phase with Al) has been reiterated in several subsequent studies.^{8, 43, 48} For instance, Shen et al.^{43, 48} proposed that Al and V are rejected from hydride precipitates to the matrix where they form Al rich or V rich regions. The Al or V enriched regions subsequently stabilise Ti_3Al or beta phases respectively. Shen et al.^{43, 48} interpreted that the rejection of Al and V from hydride precipitates occurs during hydrogenation induced disproportionation.⁴⁸

The summarised studies^{8, 21, 37, 38, 43, 48, 53} make advances that enhance the general understanding of hydrogen promoted Ti_3Al precipitation. It is now understood that alloyed hydrogen can contribute to Ti_3Al precipitation by combined effects from its beta stabilising effect, and hydride precipitation. The contributions from the beta stabilising effect are easier to predict because it is well articulated in Ti-6Al-4VxH literature. On the contrary, the contributions from hydrides are mentioned but they largely remain unclear.

The proposed rejection of Al and V from hydrides gives perspective on the microstructure evolution events which precede grain refinement. Hydrides can precipitate within a coarse alpha grain; Al and V would be rejected to enrich part of the matrix of the coarse alpha grain, and nanosized Ti_3Al and refined beta grains would subsequently nucleate at the enriched regions. Therefore, temporary hydrogen treated microstructures would have characteristic refined beta grains and nanosized Ti_3Al which nucleated within a coarse parent alpha grain.

The nucleation of refined grains within a coarse parent grain has been observed in Ti-6Al-4V microstructures which underwent different temporary hydrogen treatments; HDH,⁴⁸ THP-BD^{8, 39} and THP-MD.⁴⁵ **Figure 2.5 a-d)** shows a montage of refined microstructures which were treated using a, b) THP-MD and c, d) THP-BD treatments. The starting microstructures before the THP-MD and THP-BD treatments were bimodal and Widmanstätten respectively. In **Figure 2.5**, the optical micrographs show a) coarse martensite plates and c) coarse alpha grains. Their corresponding bright field TEM micrographs b, d) show finer grains which nucleated within the coarse parent grains.

2.6.2.1 Note on vanadium (V) rejection from hydrides

Figure 2.5 e) is a [001] zone axis SAD pattern confirming a beta grain which nucleated within a coarse alpha grain. **Figure 2.5 e)** can support the proposed idea of V rejection from hydrides when interpreting that V was rejected from fine hydride precipitates to the adjacent matrix region where it stabilised nanosized beta phase. This idea can be validated by mapping the V concentration at hydrides and their adjacent matrix regions.

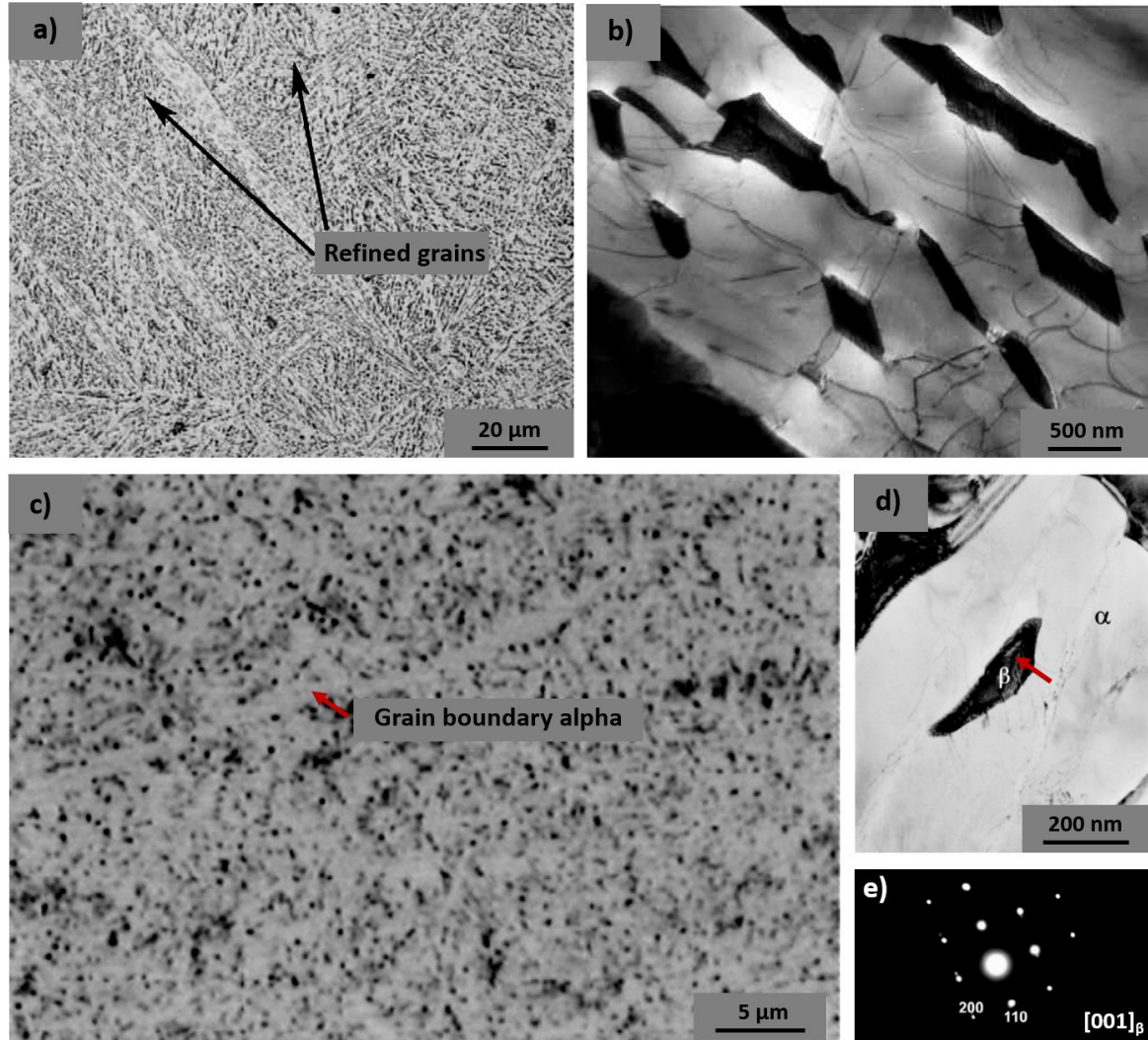


Figure 2. 5: a, c) Optical and b, d) bright field TEM micrographs of a, b) THP-MD treated⁴⁵ and c, d) THP-BD treated³⁹ Ti-6Al-4V. Temporary hydrogen treatment promoted grain refinement within a) coarse martensite plates and c) coarse alpha grains. The [001] SAD pattern in e) ³⁹ was attained from the highlighted grain in d) and it confirms that refined beta phase nucleated within alpha during THP-BD treatment.

It is understood that hydride precipitates induce volume misfits of 8-11% in beta and 0-5% in alpha respectively.⁵¹ The volume misfits distort the lattice, and are accommodated by plastic deformation of the matrix region surrounding hydrides.⁵¹ Hydride induced deformation was investigated by Shan et al.⁵¹ However, its effect on the nucleation of refined grains had not been demonstrated at atomic resolution until recently.

Tsai and Wang⁵² recently documented the contribution of hydrides to the nucleation of refined grains. They⁵² argued that hydride precipitation causes stacking faults, twinning and misfit dislocations which become nucleation sites for refined grains, and validated it using atomic resolution TEM information from hydrogenated and dehydrogenated Ti-6Al-4V.

Figure 2.6 a-e) shows a, b) bright field TEM micrographs of misfit dislocations (white arrows). The HRTEM micrograph in c) and its corresponding Fast Fourier Transform in d) which is indexed in e) confirms a nanosized Ti_3Al precipitate at a $[11\bar{2}0]$ zone axis; the nanosized Ti_3Al precipitate is adjacent to a misfit dislocation. **Figure 2.7 a-c)** similarly confirms nanosized Ti_3Al and alpha grains at $[11\bar{2}0]$ and $[11\bar{2}3]$ zone axes respectively. The nanosized grains are bordered by ill-defined lattice regions which are interpreted as diffusion channels for Ti, Al and V atoms between the nucleated grains. The close proximity of the refined grains to the misfit dislocations or ill-defined lattice regions supports hydride induced defects acting as nucleation points for refined grains.⁵²

2.6.2.2 Note on aluminium rejection from hydrides

Figure 2.7 a-c) shows nanosized Ti_3Al and alpha grains that are separated by an ill-defined lattice region. **Figure 2.7 a-c)** can support the proposed idea of Al being rejected from hydrides when interpreting the sequence that hydrides induced misfit dislocations in adjacent matrix regions; aluminium was rejected from hydrides to enrich adjacent matrix regions; hydrides decomposed to alpha during dehydrogenation and nanosized Ti_3Al grains nucleated at the Al rich regions which were adjacent to misfit dislocations. This evolution mechanism can result in a microstructure that has nanosized Ti_3Al and alpha grains which are separated by an ill-defined lattice region. This idea can be validated by mapping Al distribution at hydrides and their adjacent matrix regions.

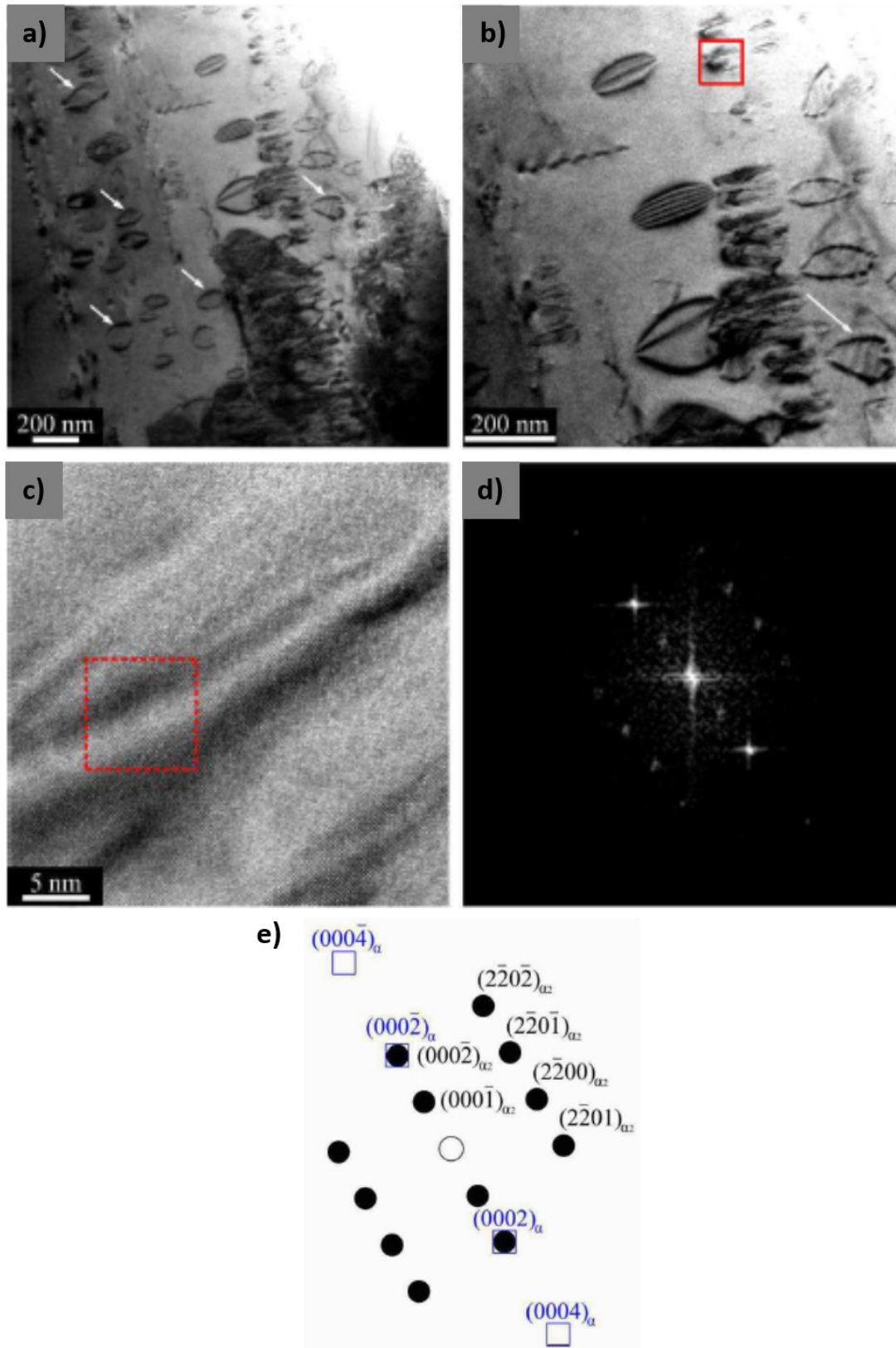


Figure 2. 6: a, b) Bright field TEM showing misfit dislocations (white arrows) in hydrogenated (to 10 at.%H) and dehydrogenated (at 600°C) Ti-6Al-4V. Images c-d) show c) an HRTEM micrograph of the highlighted region in b) and d) a Fast Fourier Transform of the highlighted region in c) which is indexed in e) and it confirms Ti_3Al at a $[11\bar{2}0]$ zone axis. Images a-e) demonstrate that refined Ti_3Al nucleates at hydrogen induced misfit dislocations. ⁵²

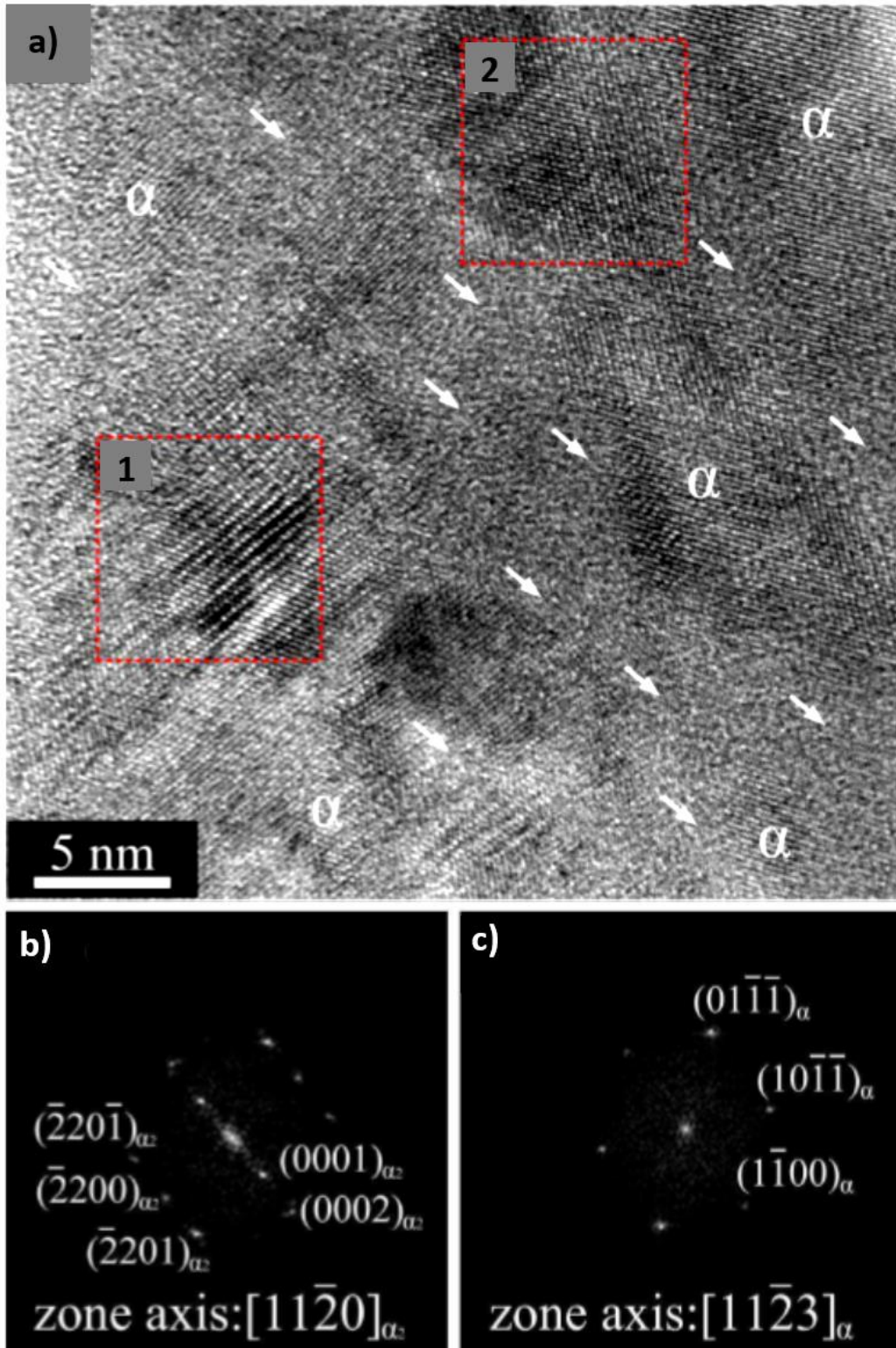


Figure 2. 7: a, b) HRTEM micrograph of Ti-6Al-4V hydrogenated (to 20 at.% H) and dehydrogenated (at 600°C) highlighting (in red) regions of interest 1,2 which are adjacent to an ill-defined lattice region (white arrows). Images b, c) are fast Fourier transforms of regions 1, 2 in a) respectively. They confirm Ti_3Al and alpha phases at zone axes $[11\bar{2}0]$ and $[11\bar{2}3]$ respectively. Images a-c) demonstrate that the adjacent hydride induced microstructure imperfections (ill-defined regions) were nucleation sites for the refined Ti_3Al grains.⁵²

2.6.3 Insights provided by published literature

Research published in the open literature has made significant advances towards understanding hydrogen promoted microstructure evolution. In summary, it is known that refined grains nucleate within coarse parent grains at hydride induced microstructure imperfections. It is predicted that Al and V are rejected from hydrides during hydrogenation promoted disproportionation, and the rejected Al and V concentrates in adjacent matrix regions to stabilise Ti_3Al and beta grains respectively.^{43, 48} However, there are some contributions which can be made to improve the understanding of hydrogen promoted microstructure evolution and its effects on tensile performance. For instance:

- A useful contribution can be made to the prediction that Al and V is rejected from hydrides to the matrix where they form Al rich and V rich regions that stabilise Ti_3Al and beta phases respectively.⁴⁸ The useful contribution would be to validate the latter by mapping the phase constitution and elemental composition at hydrides and their surrounding regions.
- A useful contribution can be made to the interpretation that hydrides reject Al and V during hydrogenation promoted disproportionation.⁴⁸ This interpretation is supported by referencing that hydrogenation induced disproportionation is common in many alloy systems.⁴⁸ However, hydrogenation-disproportionation has not been microstructurally validated in the Ti-6Al-4V context. A useful contribution would be to explore the extent to which the hydrogenated Ti-6Al-4V microstructure exhibits hydrogenation-disproportionation.
- A useful contribution can be made to the interpretation that improved hardness indicates the “improved mechanical performance” of hydrogen treated microstructures.⁵² Titanium aluminide (Ti_3Al) precipitates increase hardness; this can give a false measure of improved mechanical performance which undermines the detrimental effects that Ti_3Al precipitates can have on room temperature tensile ductility. A necessary contribution to literature would be to evaluate the effect of Ti_3Al on room temperature tensile performance in order to establish the processing parameters that control Ti_3Al embrittlement.

2.7 Summary of the gap in literature

The argument presented in this work exposes the unreliable representation of the Ti_3Al phase in grain refinement by temporary hydrogen treatment literature (as outlined in **Section 2.5**). This literature shows that hydrogen promotes grain refinement, and in some unclear circumstances it also promotes Ti_3Al phase precipitation. The unreliable representation was linked to the 1980-2001 Ti-6Al-4VxH phase diagrams which did not document Ti_3Al as a hydrogen induced phase. Consequently, the grain refinement by temporary hydrogen treatment frameworks that were proposed at the time did not account for Ti_3Al precipitation.

The recent Ti-6Al-4VxH phase diagram was published in 2015, and it proposed both hydrides and Ti_3Al as hydrogen induced phases. This phase diagram exposes gaps in the existing microstructure evolution frameworks (the repeated nucleation framework). It challenges Ti-6Al-4V hydrogen research to propose new microstructure evolution frameworks that account for Ti_3Al precipitation. It is important to investigate Ti_3Al precipitation in hydrogenated Ti-6Al-4V because Ti_3Al can deteriorate the improved property benefits that are expected from hydrogen refined microstructures.

The Ti-6Al-4VxH literature has also made some significant advances towards understanding hydrogen promoted microstructure evolution. It has demonstrated at atomic resolution that hydrides induce microstructure imperfections (dislocation loops, twins, and stacking faults) which act as nucleation points for refined grains. However, some of the proposed ideas on hydrides promoting Ti_3Al precipitation have not been microstructurally demonstrated. Consequently, existing Ti-6Al-4VxH literature does not fully explore these aspects of the Ti_3Al discourse:

- The effect of hydrogen on Ti_3Al precipitation.
- The extent to which Ti_3Al precipitates are detrimental to the tensile performance.
- The optimisation of grain refinement by temporary hydrogen treatment to control Ti_3Al embrittlement.
- The microstructure evolution framework for temporary hydrogen treated Ti-6Al-4V that accounts for the evolution of grain refinement and centralises the intimate relationship between hydrogen and Ti_3Al .

2.8 Emerging perspectives on microstructure evolution in hydrogen treated Ti-6Al-4V

In 2005, 2009 Funayama et al. and Iwaki et al.^{54, 55} introduced a different perspective of thinking about microstructure evolution in hydrogen treated Ti-6Al-4V. They noted the grain refinement in Yoshimura and Nakahigashi's studies^{9,11} and alluded that the hydrogenation-disproportionation-desorption-recombination (HDDR) framework governed microstructure evolution instead of their quoted repeated nucleation framework.^{9, 11}

The HDDR framework is not new, but its association with microstructure evolution in hydrogen treated Ti-6Al-4V is a recent occurrence (2005, 2009).^{54, 55} The HDDR framework was introduced by Takeshita and Nakayama¹³ in 1989 to interpret microstructure evolution in hydrogen treated Nd-Fe-B alloys.¹³ The HDDR framework has been primarily centralised in the Nd-Fe-B grain refinement by temporary hydrogen treatment discourse. However, its recent association with Ti-6Al-4V^{54, 55} has prompted some Ti-6Al-4VxH researchers to adopt the disproportionation component of HDDR to validate Ti_3Al precipitation in hydrogen treated Ti-6Al-4V.^{43, 48, 49, 56} This adoption means that the perspectives of some researchers are shifting towards the idea of HDDR governing microstructure evolution in hydrogen treated Ti-6Al-4V. However, this shift in perspective uncovers another gap in literature where microstructural evidence is required to confirm that the HDDR framework explains microstructure evolution in hydrogen treated Ti-6Al-4V.

In summary, Ti-6Al-4V hydrogen research has not explored microstructure evolution using an HDDR perspective. It has gone as far as adopting the disproportionation aspect of HDDR to justify Ti_3Al precipitation in hydrogen treated Ti-6Al-4V.^{43, 48, 49, 56} Therefore there is no microstructure evidence which confirms HDDR in hydrogen treated Ti-6Al-4V.

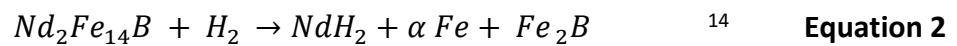
It is important to understand the key features of disproportionated or recombined microstructures in order to justify the occurrence of HDDR in hydrogen treated Ti-6Al-4V. However, HDDR information is not available for Ti-6Al-4V alloys, and therefore **Section 2.8.1** will use an Nd-Fe-B alloy to highlight the key features of disproportionated and recombined microstructures.

2.8.1 Hydrogenation-disproportionation-desorption-recombination (HDDR): An Nd-Fe-B case study

The HDDR perspective offers a comprehensive analysis of microstructure evolution during hydrogen absorption (disproportionation) and subsequent desorption (recombination).

2.8.1.1 The disproportionated Nd-Fe-B microstructure

Two phases play a critical role in hydrogen promoted microstructure evolution in the Nd-Fe-B alloy; a grain boundary Nd-rich phase and a matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Hydrogen is initially absorbed by the grain boundary Nd-rich phase to precipitate a neodymium hydride (NdH_2).⁵⁷ This is an exothermic reaction that promotes hydrogenation of the matrix phase $\text{Nd}_2\text{Fe}_{14}\text{B}$. **Equation 2**¹⁴ explains HDDR in Nd-Fe-B alloys: absorbed hydrogen in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase precipitates a neodymium hydride (NdH_2) which partitions ferrite ($\alpha\text{-Fe}$) from its high affinity element (Nd).¹⁴ The partitioned ferrite concentrates in some regions of the microstructure. This results in a microstructure that has Fe-rich and Fe-lean regions which stabilise ferrite ($\alpha\text{-Fe}$) and ferrobordinate (Fe_2B) phases respectively.



Hydrogenation-disproportionation is represented in **Figure 2.8 a, b)** which show a) partially and b) fully disproportionated $\text{Nd}_2\text{Fe}_{14}\text{B}$ microstructures. A partially disproportionated microstructure consists of: NdH_2 precipitates, ferrite ($\alpha\text{-Fe}$), ferrobordinate (Fe_2B) and a remnant $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase that has not decomposed to $\alpha\text{-Fe}$ and Fe_2B . In comparison, a fully disproportionated microstructure is fully decomposed and it has no remnant $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

Figure 2.9 a, b) shows a disproportionated Nd-Fe-B microstructure at atomic resolution.⁵⁸ **Figure 2.9 a)** shows the neodymium hydride (NdH_2) and ferrite ($\alpha\text{-Fe}$) regions in a fully disproportionated microstructure and **Figure 2.9 b)** shows their complementary nanobeam diffraction patterns attained at the: i) hydride region (NdH_2), ii) hydride and ferrite interface ($\text{NdH}_2/\alpha\text{-Fe}$) and iii) ferrite region ($\alpha\text{-Fe}$). Nanobeam diffraction patterns from hydride and ferrite regions show distinct atomic columns of hydride and ferrite. There is no distinct phase at the interface, it has superimposed patterns of the abovementioned phases. This implies that hydrides disproportionate the matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase to form ferrite rich and ferrite lean regions.

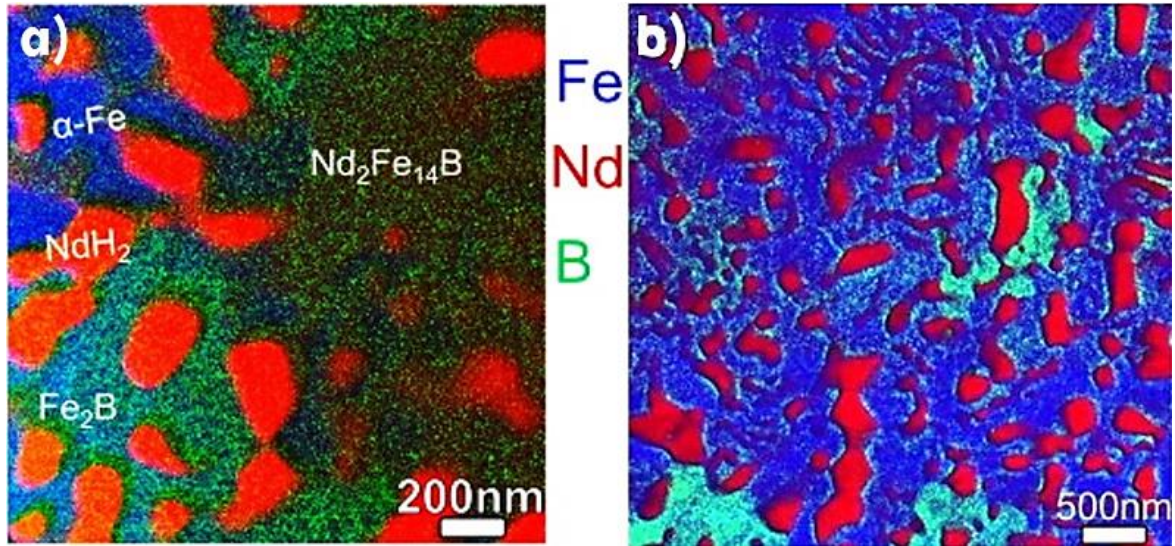


Figure 2. 8: *a, b*) Superimposed EFTEM micrographs showing a) partially and b) fully disproportionated microstructures. In a) the partially disproportionated microstructure has remnant $\text{Nd}_2\text{Fe}_{14}\text{B}$ whilst its fully disproportionated counterpart has Nd-rich (red), Fe-rich (blue) and B-rich (green) regions which are NdH_2 , $\alpha\text{-Fe}$ and Fe_2B phases respectively.⁵⁸

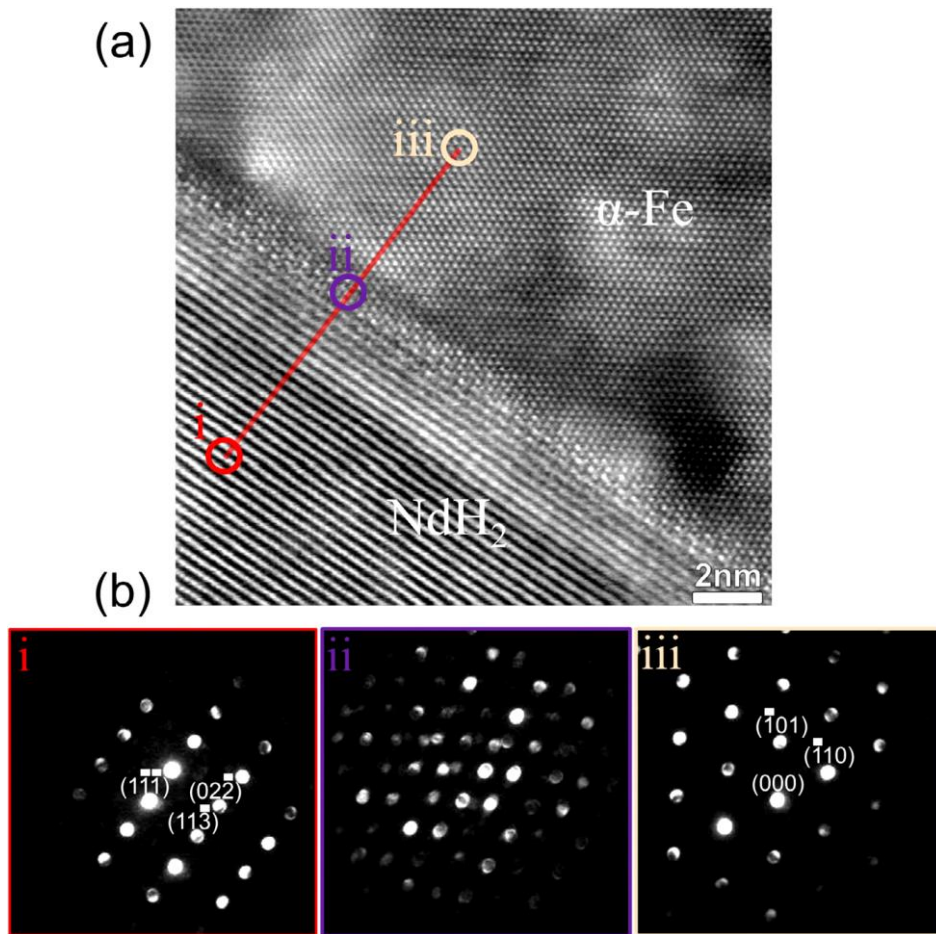


Figure 2. 9: a) Atomic resolution HAADF STEM micrograph and b) nanobeam diffraction patterns attained from i) NdH_2 , ii) $\text{NdH}_2/\alpha\text{-Fe}$ interface and iii) $\alpha\text{-Fe}$ regions of a fully disproportionated microstructure.⁵⁸

2.8.1.2 The recombined Nd-Fe-B microstructure

Microstructure recombination is a diffusion controlled reversal of the disproportionation reaction that occurs when hydrogen is removed at high temperature. Microstructure recombination has been proposed to occur through the Nd-rich island model.¹⁴ This model states that hydrogen desorption decomposes NdH_2 to form Nd-rich islands.¹⁴ These subsequently recombine with surrounding $\alpha\text{-Fe}$ to nucleate refined $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains.

The processing conditions (time and temperature) determine the extent of microstructure recombination. Inadequate processing conditions result in partially recombined microstructures that have remnant disproportionation products.¹⁴ For this reason, partially recombined microstructures have been used to confirm the Nd-rich island model. **Figure 2.10** shows a 3D tomograph of a partially recombined microstructure. **Figure 2.10** validates the Nd rich island model because it shows recombined $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains surrounding Nd rich regions. However, the nucleation interface of the refined $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains is still contested between the Nd rich/ Fe^{14} or the Nd rich/ Fe_2B interfaces.⁵⁸ This is because the former does not explain the supply of boron to the growing $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain.

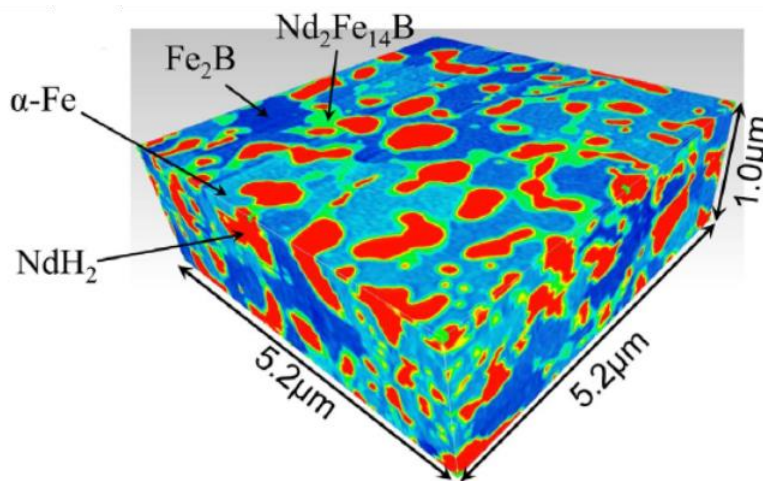


Figure 2. 10: 3D SEM tomography of a ($5.2 \times 5.2 \times 1 \mu\text{m}$) partially recombined microstructure showing NdH_2 (red), $\alpha\text{-Fe}$ (light blue), Fe_2B (dark blue) and recombined $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (green).⁵⁸

In summary, the recombined microstructure has refined grains which nucleate when disproportionation products decompose. The extent of recombination depends on processing parameters; hydrides decompose after hydrogen escape but the ferrite rich regions (caused by disproportionation) require sufficient $\alpha\text{-Fe}$ diffusion to fully recombine with Nd.

2.9 Documented variations of the HDDR framework

In 1989 Takeshita and Nakayama¹³ developed a hydrogenation-dehydrogenation treatment that refined the grain size and consequently improved the coercivity of a magnetic Nd-Fe-B alloy ingot.¹³ This process was subsequently defined as hydrogenation-disproportionation-desorption-recombination (HDDR) by Harris and McGuiness in 1991.⁵⁹ Between 1992 and 1996, several publications took on this definition when interpreting microstructure evolution in hydrogen treated Nd-Fe-B.^{60, 61}

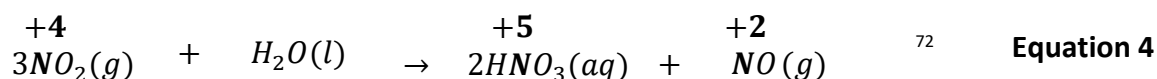
More interestingly, in the same period (1992-1996) Takeshita and Nakayama⁶²⁻⁶⁵ with other authors⁶⁶⁻⁶⁸ defined HDDR as hydrogenation-decomposition-desorption- recombination. In some instances, the words disproportionation and decomposition were used interchangeably in one publication⁶⁹ or in a series of publications from the same author.⁷⁰ Takeshita and Nakayama did not elaborate on their preference to define HDDR using decomposition instead of disproportionation. However, this could mean the words disproportionation and decomposition were used interchangeably to infer the same meaning. It could also mean the word disproportionation was avoided because it had adapted definitions (in different disciplines) which could distort the manner in which the intended meaning (in this current context) was perceived.

2.9.1 Defining disproportionation

The International Union of Pure and Applied Chemistry (IUPAC) describes a disproportionation reaction as a chemical reaction where a molecule transforms into two or more dissimilar products that are different chemical species.⁷¹ This is described by **Equation 3** where A, A' and A'' are different chemical species.



Disproportionation also occurs in redox reactions, when one element is simultaneously oxidised and reduced to form at least two different products.⁷¹ An example of a disproportionation redox reaction is presented in **Equation 4** where N (+4) is simultaneously oxidised and reduced to oxidation states of +5 and +2 respectively.



Within the context of redox reactions, the word disproportionation also defines a transition in which species with the same oxidation state combine to yield one of higher oxidation state and one of lower oxidation state.⁷³ This is described by **Equation 5** where Au⁺ combines to yield products of higher (Au³⁺) and lower (2Au) oxidation states.

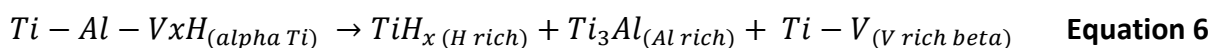


The chemistry adaptations of disproportionation can confuse meaning when disproportionation is used in metallurgy. This problem can be compounded by the fact that disproportionation products or phases (in metallurgy) do not always have definitive stoichiometric structures.

Therefore the present work defines disproportionation according to **Equation 1**; a chemical reaction where a molecule transforms into two or more dissimilar products that are different chemical species.⁷¹ Aspects of this definition can be found in Nd-Fe-B literature where disproportionation is described as a eutectoid-type⁵⁷ transformation that is initiated by hydrogen absorption, and it yields ferrite rich (α -Fe) and boron rich (Fe₂B) phases. In hindsight, this description aligns with the interchangeable use of disproportionation and decomposition (that has been observed in literature) because a eutectoid-type transformation can be described as a decomposition.

2.10 An idea of the hydrogenation-disproportionation reaction in the Ti-6Al-4V context

The literature shows that hydrogen treated Ti-6Al-4V microstructures have refined BCC grains and nanosized Ti₃Al precipitates which nucleate within coarse alpha grains (**Section 2.6.2.1**). Therefore an idea of a hydrogenation-disproportionation reaction in the Ti-6Al-4V context can be described by **Equation 6** where hydrogenation transforms alpha titanium into two or more products (Ti₃Al and beta) that have different chemical composition (Al rich or V rich). This is predicted to proceed through a rejection of Al and V from hydride precipitates to adjacent matrix regions, where they form Al and V enriched regions which stabilise Ti₃Al and beta phases respectively.^{43, 48}



Since hydrogenation-disproportionation^{43, 48} is proposed to proceed through the rejection of Al and V from hydride precipitates, and the degree of recombination is determined the desorption temperature. Evaluating HDDR in Ti-6Al-4V will require an understanding of the effect of temperature on the diffusivity of Al, V, and H atoms.

2.10.1 The diffusivities of hydrogen, aluminium and vanadium in alpha and beta titanium

The effect of temperature on the diffusivity of hydrogen in alpha (D_α) and beta (D_β) titanium is defined by **Equations 7** and **8** respectively. These equations are plotted in **Figure 2.11**^{50, 75, 76} and compared to the elevated temperature diffusivity values of Al and V.

The diffusivity of Al and V in alpha and beta titanium is slower than the diffusivity of hydrogen. The Al and V diffusivity ranges from 10^{-16} (m^2/s) to 10^{-14} (m^2/s) between 800°C and 900°C .⁷⁴⁻⁷⁶ At the same temperature range, hydrogen has a comparatively higher diffusivity of 10^{-9} (m^2/s). It can also be inferred from **Figure 2.11** that the Al and V diffusivity is negligible at room temperature.⁷⁵ Therefore sufficient annealing time is required to promote Al and V diffusion especially at low annealing temperatures.

$$D_\alpha = 1.8 \times 10^{-6} \exp(-6230/T) \quad 50, 75, 76 \quad \text{Equation 7}$$

$$D_\beta = 1.8 \times 10^{-7} \exp(-3342/T) \quad 50, 75, 76 \quad \text{Equation 8}$$

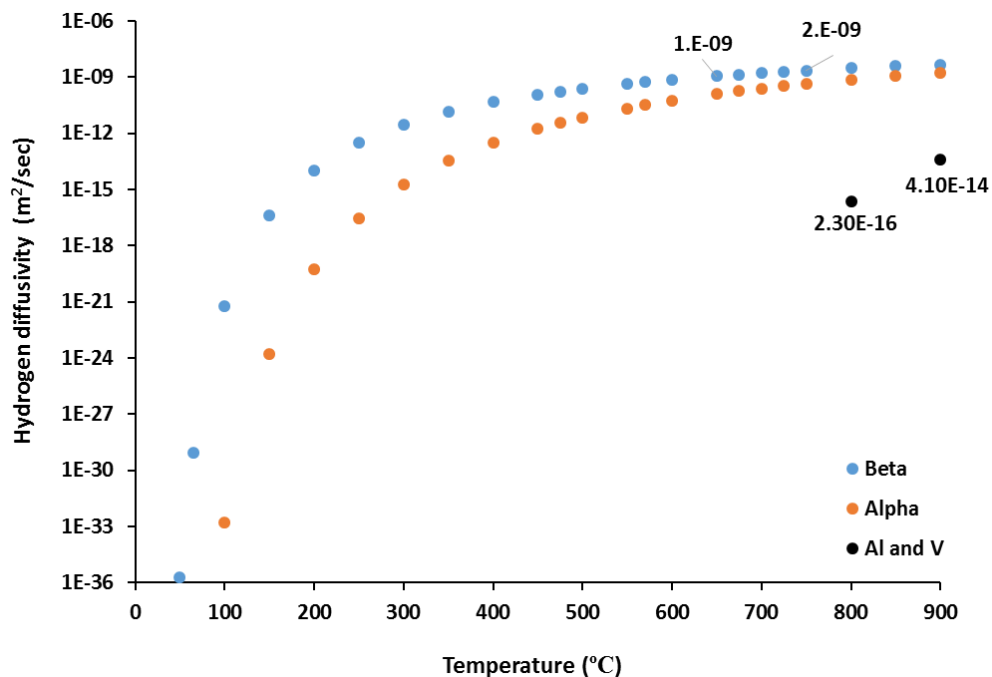


Figure 2. 11: The effect of temperature on the diffusivity of hydrogen, Al and V.^{50, 75, 76}

2.10.2 Hydride precipitation in alpha

Three types of titanium hydrides are reported in literature: FCT- γ (or Ti-H) hydride ($c/a > 1$), FCC- δ (or Ti-H₂) hydride ($c/a = 1$) and FCT- ϵ hydride ($c/a < 1$).⁷⁷ The FCT- γ hydride precipitates at low hydrogen concentrations. The FCC- δ hydride is a medium hydrogen bearing hydride which precipitates at hydrogen concentrations of TiH_x (where x is between 1.5 and 2).⁷⁷ The FCT- ϵ hydride ($c/a < 1$) precipitates at high hydrogen concentrations that are above the limiting composition of TiH₂.⁷⁷ In this instance, the FCC- δ hydride undergoes a room temperature distortion to the less symmetrical tetragonal hydride FCT- ϵ to lower its energy.⁷⁸ The FCT- ϵ ($c/a < 1$) phase has the lowest energy and has been experimentally observed below room temperature.^{78, 79}

Figure 2.12 illustrates the HCP alpha (space group $P63/mmc$) to FCC hydride (space group $Fm\bar{3}m$) transformation.⁸⁰ Hydrogen diffuses into either tetrahedral⁷⁷ or octahedral⁸⁰ sites of the HCP lattice. However, the tetrahedral sites are the preferred sites for the TiH₂ stoichiometry because they offer the lowest energy configuration.⁷⁸ The HCP to FCC hydride transformation proceeds through hydrogen atoms inserting into interstitial sites without changing the arrangement of titanium atoms.⁸⁰ This expands the HCP lattice, and the HCP to FCC lattice transformation occurs to accommodate lattice strain.⁵¹ The FCC hydride is considered a pseudo HCP phase that is distorted by supersaturation of hydrogen in alpha.⁵¹

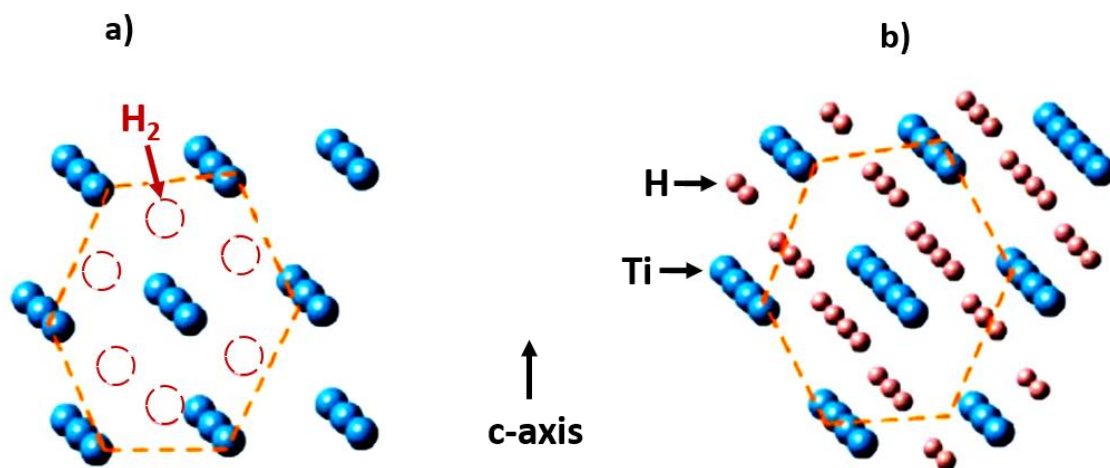


Figure 2. 12: Schematic diagrams illustrating a) the diffusion of hydrogen into octahedral interstitial sites of the HCP lattice and b) the FCC hydride precipitate.⁸⁰

2.10.3 Ti_3Al precipitation in alpha

Figure 2.13 shows the HCP crystal structures of alpha and Ti_3Al . The HCP alpha lattice has the lattice parameters; a -0.293nm, c - 0.467 nm and a c/a ratio of 1.592.⁸¹ The HCP lattice orders to precipitate Ti_3Al with a $D0_{19}$ structure and the lattice parameters: a -0.5793 nm, c -0.467 nm and a c/a ratio of 0.80.⁷⁶ This occurs when the maximum solubility of Al in the HCP alpha lattice (10 at.%Al)⁸² is exceeded. Therefore Ti_3Al precipitates in alpha have been observed from a minimum of 11 at.%Al.⁸³ Crystallographic orientation investigations show that Ti_3Al precipitates maintain parallel basal planes and the same orientation direction with the parent alpha lattice.⁴⁸ Consequently, Ti_3Al precipitates are observed to be coherent with the parent alpha lattice.⁸³

The alpha phase can accommodate up to 22% strain before fracture at room temperature because it can deform through $\langle c+a \rangle$ slip and twinning.⁸¹ In comparison, Ti_3Al has limited room temperature ductility and it accommodates less than 3% strain before fracture.⁸¹ This low ductility arises from: the absence of $\langle c \rangle$ slip, the low mobility of $\langle c+a \rangle$ dislocations and the absence of twinning.⁸¹ The absence of $\langle c \rangle$ slip and the low mobility of $\langle c+a \rangle$ dislocations contribute to stress accumulation at grain boundaries which is a precursor to fracture. Moreover, twinning does not occur in Ti_3Al because it causes a disorder that is incompatible with the ordered Ti_3Al crystal.⁸¹ Notwithstanding this, Ti_3Al precipitates yield high strength performance at elevated temperatures between 500°C to 700°C.⁸¹

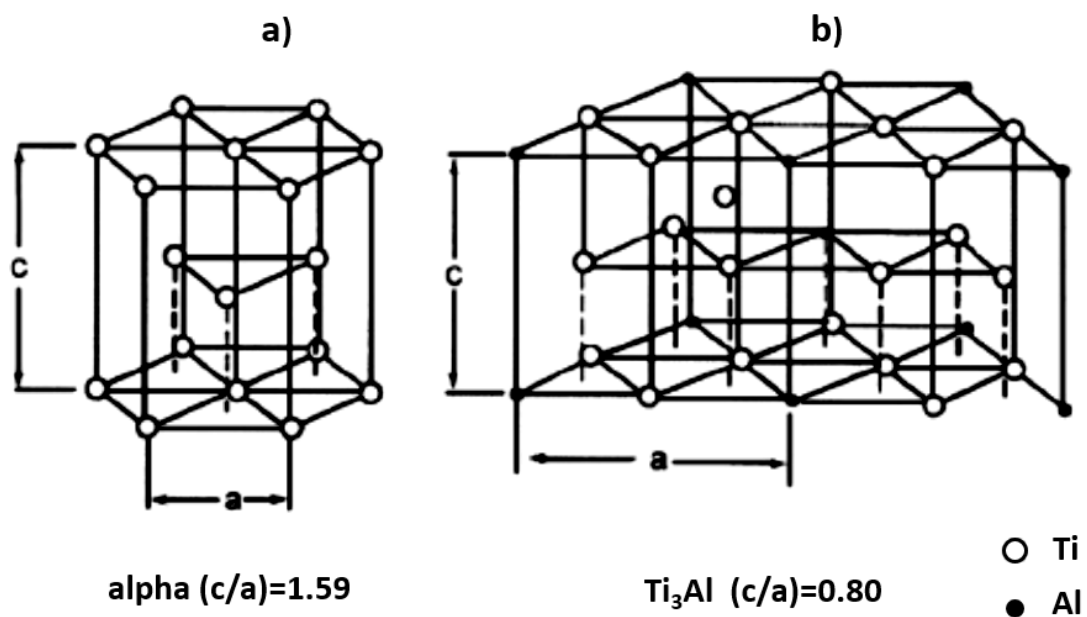


Figure 2. 13: Crystal structures of a) alpha and b) Ti_3Al .⁸¹

2.10.4 Legitimacy of the HDDR framework in hydrogen treated Ti-6Al-4V

It is reasonable to consider that the HDDR framework better accounts for microstructure evolution in hydrogen treated Ti-6Al-4V compared to the repeated nucleation framework. Although both frameworks (HDDR and repeated nucleation) communicate that submicron grain refinement results from hydride promoted nucleation, they articulate hydrogen promoted microstructure evolution differently.

The repeated nucleation framework does not holistically articulate hydrogen promoted microstructure evolution, it is often employed in inverse optimisation studies (**Section 2.4.2.2**) and has perpetuated the Ti_3Al gap. The HDDR framework can address the Ti_3Al gap because it holistically articulates hydrogen promoted microstructure evolution as elaborated in **Sections 2.10.4.1** and **2.10.4.2**.

2.10.4.1 HDDR provides discourse on Ti_3Al formation in hydrogen treated Ti-6Al-4V

The repeated nucleation framework highlights the influence of hydrides on grain refinement (hydride promoted nucleation causes submicron grain refinement). In addition to this, the HDDR framework elaborates on the influence of hydrides on phase evolution. Therefore it can provide the discourse on Ti_3Al formation that is not articulated by the repeated nucleation framework.

2.10.4.2 HDDR accounts for submicron grain refinement in alloys that have hydride forming elements

The HDDR framework has been reported to cause submicron grain refinement in other alloy systems that have hydride forming elements ^{55, 84} like neodymium,⁸⁵ magnesium,⁵⁴ and zirconium alloys. ⁸⁶ These studies attribute the submicron grain refinement to the microstructure changes that occur during hydrogenation-disproportionation and desorption-recombination. Similarly, the Ti-6Al-4V alloy also has a hydride forming element (titanium) and it undergoes substantial refinement (submicron grain refinement) during hydrogen treatment.^{9-11, 18, 19} Therefore, it is reasonable to think that the HDDR framework or aspects of the HDDR framework can account for the evolution of grain refinement in hydrogen treated Ti-6Al-4V.

2.11 Objectives, hypotheses and research questions

The objectives of this thesis are to:

- Use hydrogen to promote microstructure refinement, optimise tensile performance but avoid the concomitant Ti_3Al embrittlement.
- To thoroughly investigate the influence of hydrogen on Ti-6Al-4V microstructure evolution in order to uncover the intimate relationship between hydrogen and Ti_3Al .
- To propose a microstructure evolution framework for hydrogen treated Ti-6Al-4V that accounts for the evolution of grain refinement and centralises the intimate relationship between hydrogen and Ti_3Al .

This thesis hypothesises that:

- Grain refinement of Ti-6Al-4V by temporary hydrogen alloying can cause embrittling effects which remain even when hydrogen is fully expelled from the alloy.
- The hydrogenation-disproportionation-desorption-recombination (HDDR) framework can account for the evolution of grain refinement and explain the promotion of Ti_3Al formation in hydrogen treated Ti-6Al-4V.

This thesis examines whether HDDR accounts for the evolution of grain refinement in hydrogen treated Ti-6Al-4V by addressing the following research questions:

1. To what extent does the hydrogenated microstructure reflect disproportionation?
2. To what extent does the desorbed (dehydrogenated) microstructure reflect recombination?
3. What is the effect of desorption (dehydrogenation) temperature on microstructure recombination and the room temperature tensile performance?
4. What is the influence of hydrogen tempering on martensite evolution and the tensile performance of THP treated Ti-6Al-4V?
5. What is the influence of hydrogen tempering on martensite evolution and the degree of grain refinement in THDP treated Ti-6Al-4V?

The research questions are addressed in three different temporary hydrogen treatments: hydrogenation-dehydrogenation (HDH), thermohydrogen processing (THP), thermohydrogen and deformation processing (THDP) whose protocols are detailed in **Chapter 3**.

CHAPTER 3: EXPERIMENTAL METHODS

3.1 Simulated cast Ti-6Al-4V

The as-cast Ti-6Al-4V microstructure was simulated to avoid the inhomogeneity and porosity defects that are associated with castings. Wrought Ti-6Al-4V was converted to simulated cast Ti-6Al-4V by vacuum annealing at 1100°C for 2 hours. This was done to emulate the as-cast Ti-6Al-4V microstructure by growing the grain size (to diameter 2mm) and forming the Widmanstätten morphology. Therefore, simulated cast Ti-6Al-4V has a similar grain size and morphology to as-cast Ti-6Al-4V. **Figure 3.1** shows the coarse grain sizes of simulated cast Ti-6Al-4V which are similar to as-cast Ti-6Al-4V.

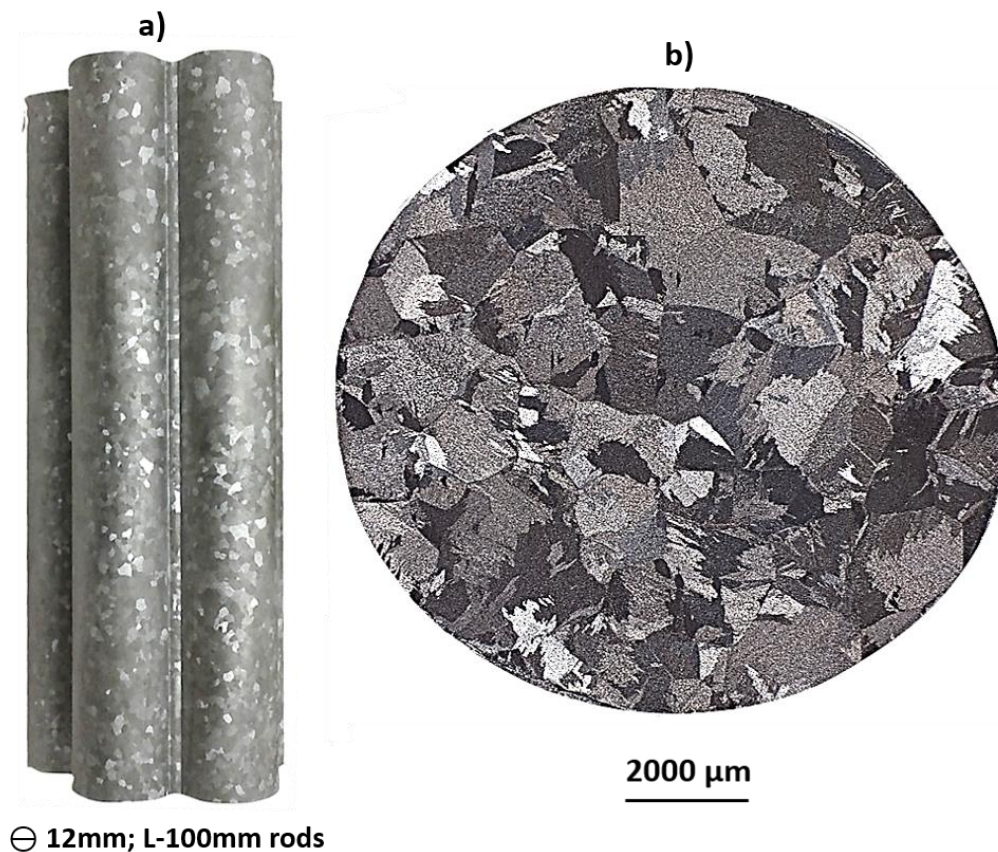


Figure 3.1: a) 12mm diameter, 100mm length simulated cast rods b) a 10mm diameter cross section showing the coarse grained simulated cast microstructure.

Grain refinement by temporary hydrogen alloying treatments were subsequently performed on simulated cast Ti-6Al-4V to refine the microstructure (grain size and morphology) in order to improve tensile performance.

3.2 Grain refinement by temporary hydrogen alloying treatments

The grain refinement by temporary hydrogen alloying treatments that were performed on simulated cast Ti-6Al-4V are: hydrogenation (H), hydrogenation-dehydrogenation (HDH), thermohydrogen processing (THP) and thermohydrogen and deformation processing (THDP). The furnace setup and its hydrogenation, dehydrogenation protocols was described in a preceding study.³

3.2.1 Hydrogenation (H)

The surfaces of simulated cast Ti-6Al-4V rods was initially cleaned with detergent and dried with ethanol and hot air to remove any surface grease. The cleaned simulated cast rods were hydrogenated to 20 at.%H by annealing in a positive hydrogen atmosphere at 650°C for 12 hours. The heating and cooling rates during the hydrogenation experiment were kept at 5°C/min. The weight of samples was measured before and after the hydrogenation experiment. The weight gained by hydrogenated samples was used to quantify the amount of absorbed hydrogen as shown in **Appendix A**.

3.2.2 Hydrogenation-dehydrogenation (HDH)

Simulated cast (Sim. cast) rods were hydrogenated (H) and subsequently dehydrogenated at different temperatures. A control experiment was similarly performed on vacuum annealed simulated cast rods (A. Sim. cast).

Figure 3.2 is a schematic diagram showing the processing temperatures that were used during the hydrogenation-dehydrogenation (HDH) treatment. Simulated cast rods were hydrogenated at 650°C for 12 hours and subsequently dehydrogenated for 3 hours at different temperatures: 675°C, 700°C, 725°C or 750°C. The dehydrogenation temperatures were varied to determine the optimum conditions for optimum tensile performance. Control experiments were also performed on annealed simulated cast (A. Sim. cast) rods. In this case, a set of reference samples was generated to replicate the same thermal cycles but without hydrogen. The control samples were vacuum annealed at 650°C for 12 hours and subsequently vacuum annealed at 675°C for 3 hours.

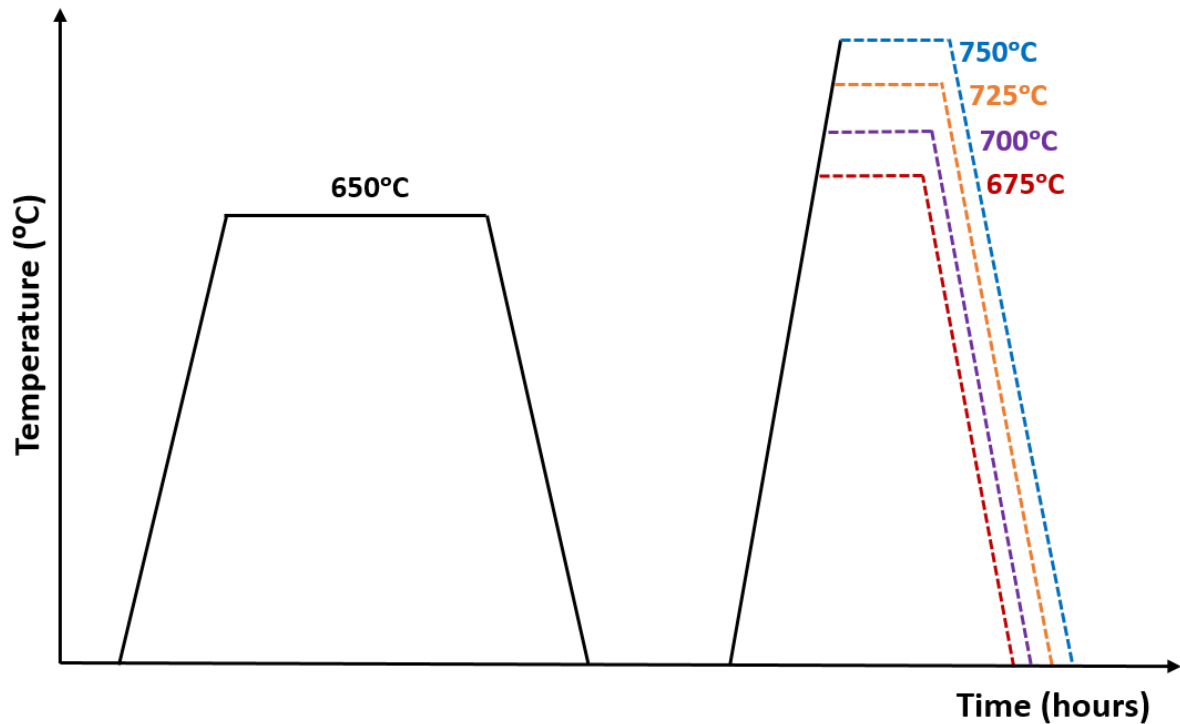


Figure 3.2: Schematic diagram showing the processing temperatures used during the hydrogenation-dehydrogenation (HDH) treatment. Simulated cast rods were hydrogenated at 650°C for 12 hours to alloy 20 at.%H. The latter were subsequently dehydrogenated for 3 hours at varied temperatures; 675°C (red), 700°C (purple), 725°C (orange) or 750°C (blue). A control treatment was also prepared to replicate the HDH 675 thermal cycle by vacuum annealing at 650°C for 12 hours and subsequently vacuum annealing at 675°C for 3 hours.

Table 3.1 shows the sample matrix of the HDH study and it shows;

- Input sample conditions (Sim. cast, H and A Sim. cast)
- HDH annealing temperatures (°C) and time (hours).

Table 3.1: HDH sample matrix showing 8 analysed sample conditions (marked x).

Dehydrogenated or vacuum annealed at Temperature (°C) – Time (hours)	Sim. cast	H	A. Sim. cast
	x	x	x
675-3		x	x
700-3		x	
725-3		x	
750-3		x	

Sim. cast: simulated cast; **H:** hydrogenated; **A. Sim. cast:** annealed simulated cast

3.2.3 Thermohydrogen processing (THP)

A thermohydrogen processing (THP) treatment was performed to study the influence of hydrogen on martensite evolution and grain refinement. Thermohydrogen processing has a series of treatment stages: hydrogenation, solution treating and quenching, aging and dehydrogenation. Solution treating and aging were performed in an argon atmosphere to prevent hydrogen escape. Dehydrogenation was performed in a vacuum atmosphere to promote hydrogen escape.

Figure 3.3 is a schematic diagram of a thermohydrogen processing (THP) procedure highlighting the processing temperatures that were used during the THP treatment. Hydrogenated rods were solution treated for an hour at 900°C and water quenched. The solution treated rods were subsequently aged for 3 hours at 580°C and quenched. After aging, the rods were dehydrogenated for 3 hours at 675°C or 750°C.

Control experiments (control 900 and control 1080) were similarly prepared by annealing non-hydrogenated rods below (900°C) or above (1080°C) the beta transus temperature. The annealed rods were similarly aged for 3 hours at 580°C and vacuum annealed for 3 hours at 675°C or 750°C.

The heating rate to all temperatures was kept at 5°C/min. A fast cooling rate (water quenching) was used at the solution treating and aging stages of the THP treatment. A furnace cooling rate of 5°C/min was used at the dehydrogenation stage of the THP treatment. The latter's heating and cooling rates were replicated at the respective stages during the control 900 and control 1080 treatments.

The Ti-6Al-4V beta transus temperature is approximately 1050°C,⁴² and thus 900°C is below the beta transus in non-hydrogenated Ti-6Al-4V. However, 900°C is above the beta transus in hydrogenated Ti-6Al-4V because 20 at.%H reduces the beta transus to approximately 800°C.⁴² Therefore the control 900 treatment results in an equilibrium microstructure whilst the THP and control 1080 treatments results in a tempered martensite microstructure. The THP and control 1080 treatments enable a comparative analysis of microstructure evolution in hydrogen tempered and non-hydrogen tempered martensite.

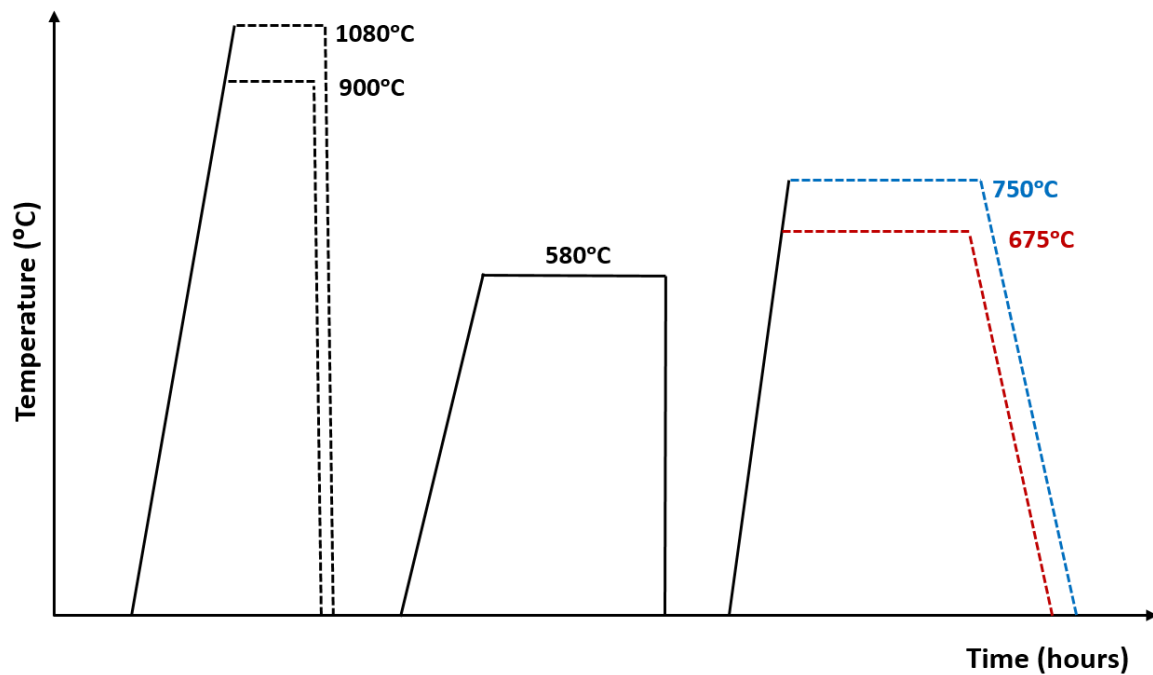


Figure 3.3: Schematic diagram of a thermohydrogen processing (THP) procedure highlighting THP treatment temperatures. Hydrogenated Ti-6Al-4V rods were solution treated for 1 hour at 900°C and quenched. They were subsequently aged for 3 hours at 580°C and dehydrogenated for 3 hours at 675°C (red) or 750°C (blue). Control experiments were similarly prepared on non-hydrogenated rods that were quenched from above (1080°C) or below (900°C) the beta transus temperature.

Table 3.2 shows the sample matrix of the THP study and it highlights:

- The performed heat treatments (Control 900, Control 1080 and THP)
- The heat treatment stages (quenched, aged and dehydrogenated or vacuum annealed)
- The heat treatment temperatures (°C) and times (hours).

Table 3.2: THP sample matrix showing 11 analysed sample conditions (marked x).

Stage - Temperature (°C) - Time (hours)	Control 900	Control 1080	THP
Quenched - 900-1	x		x
Quenched - 1080-1		x	
Aged - 580-3	x	x	x
Dehydrogenated or vacuum annealed - 675-3	x	x	x
Dehydrogenated or vacuum annealed - 750-3		x	x

3.2.4 Thermohydrogen and deformation processing (THDP)

A thermohydrogen and deformation processing (THDP) procedure was performed to study the influence of hydrogen and deformation on martensite evolution and grain refinement. The THDP process has a series of treatment stages: hydrogenation, hot deformation, recrystallisation, aging and dehydrogenation. **Figure 3.4** is a schematic diagram of a THDP procedure highlighting the processing temperatures used during the THDP treatment.

Hydrogenated samples were loaded in a Gleeble 3800 thermomechanical simulator. They were subsequently heated (at 240°C/min) to 550°C, soaked for 5 minutes and hot deformed to 1.6 true strain at a strain rate of 10s⁻¹. The deformed samples were further heated (at 240°C/min) to 900°C, recrystallised for 15 minutes and water quenched.

The recrystallized and quenched THDP samples were reheated to 580°C at a heating rate of 5°C/min, aged for 3 hours in a positive argon atmosphere (to prevent hydrogen escape) and water quenched. They were subsequently reheated in a vacuum atmosphere to 675°C and dehydrogenated for 3 hours. All dehydrogenated samples were furnace cooled at 5°C/min.

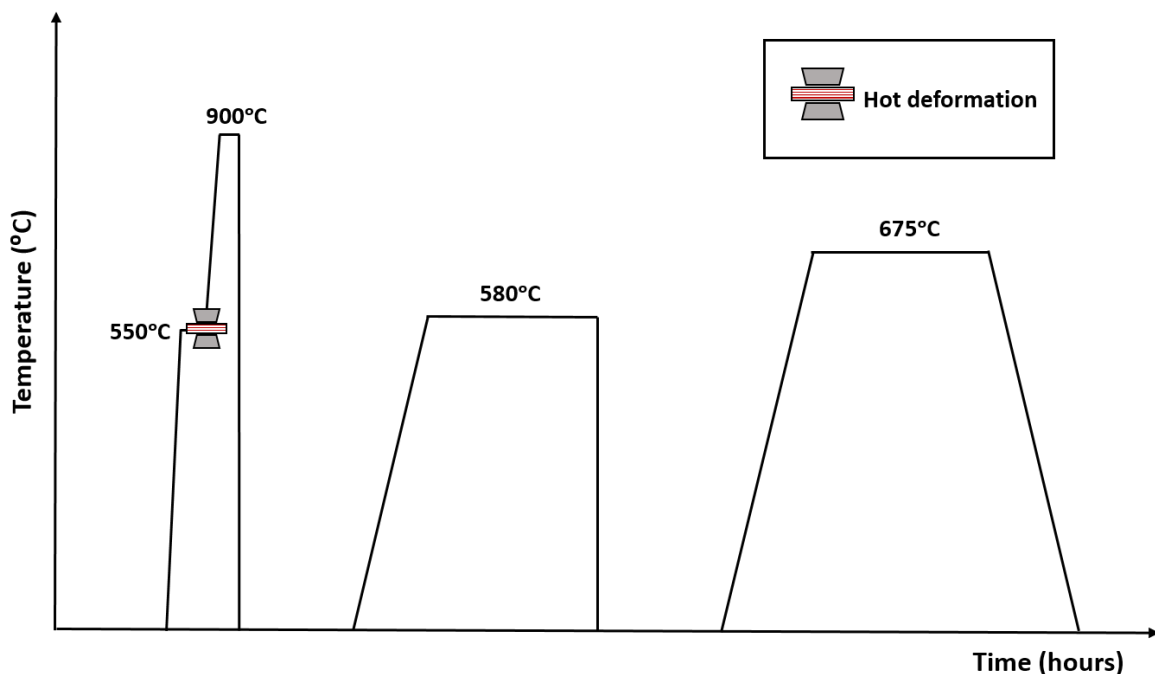


Figure 3.4: Schematic diagram of a thermohydrogen and deformation processing (THDP) procedure highlighting THDP processing temperatures. Hydrogenated THDP samples were deformed at 550°C (to 1.6 true strain, at a strain rate of 10s⁻¹), recrystallized (at 900°C for 15 minutes) and quenched. The latter were subsequently aged for 3 hours (at 580°C) and dehydrogenated for 3 hours (at 675°C).

Table 3.3 shows the THDP treatment parameters (temperature and time) and the characterised stages of the THDP treatment.

Table 3.3: THDP sample matrix showing 3 analysed sample conditions (marked x).

Stage - Temperature (°C) - Time (hours)	THDP
Deformed (1.6 true strain) and recrystallized (900-0.25) and quenched	x
Aged – 580-3	x
Dehydrogenated – 675-3	x

3.3 Tensile testing

Tensile tests were performed on a Zwick 1484 tensometer at an initial strain rate of 10^{-3}s^{-1} . All tensile tests on hydrogen treated samples were performed after hydrogen removal or dehydrogenation. All heat treated tensile rods were oversized (in diameter and length) and only configured to ASTM- E8/E8M – 13a specifications⁸⁷ after all heat treatments.

The 12mm oversized diameter was machined down to 10mm (in the grip region) and 6mm (in the gauge region) of the final tensile specimen. This removed any minor oxide contamination that may have accumulated on the sample surface during heat treatment. The 30mm oversized length provided sufficient material for subsequent microstructure analysis. All microstructure analysis was performed after eliminating the minor surface oxide contamination.

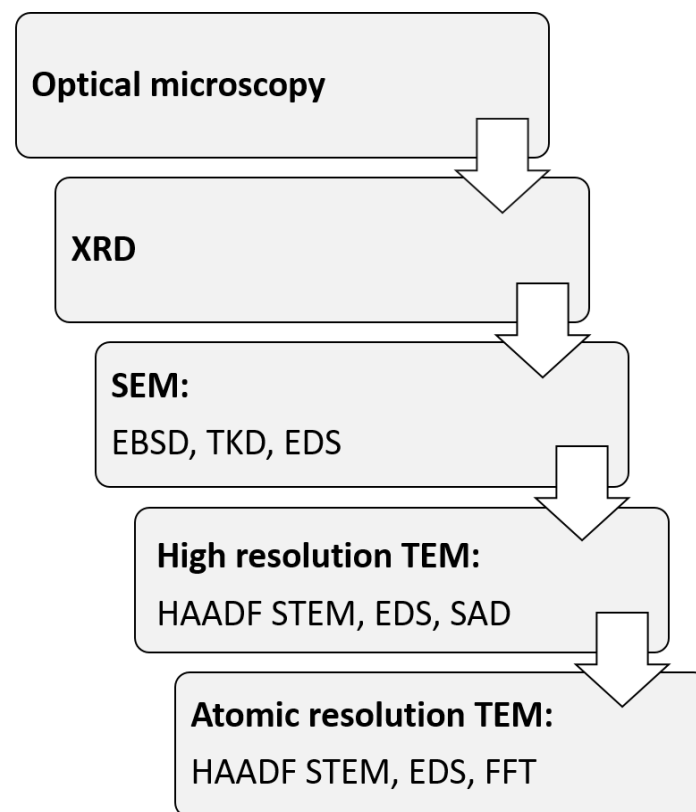
3.4 Microstructure analysis

Microstructure evolution during hydrogen treatment was investigated using complementary microstructure characterisation techniques to attain reliable evidence of the intimate relationship between hydrogen and Ti_3Al phase. Microstructure evolution was analysed from low to high resolution as guided by the flowchart in **Figure 3.5**.

Optical microscopy was performed to obtain a qualitative overview of microstructure morphology evolution during hydrogen treatment. This morphology overview was instrumental in understanding microstructure and tensile performance relationships.

X-ray diffraction (XRD) was performed to investigate phase constitution in bulk samples. The phase constitution was subsequently confirmed using electron backscatter diffraction (EBSD) and transmission Kikuchi diffraction (TKD) phase mapping in the scanning electron microscope (SEM). The effect of hydrogen alloying and hydride precipitation on aluminium (Al) partitioning and enrichment was mapped in the SEM using complementary EBSD, TKD and energy dispersive spectroscopy (EDS).

Hydrogen promoted Al partitioning and enrichment was also mapped in the transmission electron microscope (TEM) to atomic resolution. This was performed using complementary high angle annular dark field (HAADF) and EDS maps. The precipitation of Ti_3Al in Al enriched regions was confirmed using selected area diffraction (SAD) or fast Fourier transform (FFT) analyses.



XRD: X-ray diffraction; **SEM:** scanning electron microscope; **EBSD:** electron backscatter diffraction; **TKD:** transmission Kikuchi diffraction; **EDS:** energy dispersive spectroscopy; **SAD:** selected area diffraction; **TEM:** transmission electron microscopy; **STEM:** scanning TEM; **HAADF STEM:** high angle annular dark field STEM; **FFT:** fast Fourier transforms

Figure 3.5: Flowchart outlining the utilised techniques for low to high resolution microstructure characterisation.

3.4.1 Bulk phase identification using X-ray diffraction (XRD)

X-ray diffraction was used to confirm constituent phases in non-hydrogenated, hydrogenated and dehydrogenated Ti-6Al-4V. X-ray diffraction was performed in a D8 High-Resolution Diffractometer using a Cu K α radiation (wavelength 1.5405 Å) at a voltage and current of 40 kV and 40mA respectively. The XRD spectrum was obtained at a 2 theta angle of 20-100 by continuous scanning at a stepsize of 0.034° and a counting time of 10 seconds per step.

Alpha, beta and hydride phases were identified using their relevant 2 theta positions in the XRD spectra. X-ray diffraction was also useful in distinguishing titanium aluminide (Ti₃Al) from alpha phase. Alpha and Ti₃Al have the same HCP crystal structure and c-lattice parameters, therefore they cannot be distinguished by EBSD or TKD analysis. However, they have different a-lattice parameters of 0.5793nm (Ti₃Al) and 0.293nm (alpha).^{76, 81} X-ray diffraction reflects the difference in a-lattice parameters as sub-peaks on main HCP reflections.

Residual stress can also cause sub-peaking of HCP reflections; however the degree of lattice parameter change determines the position of the sub-peak from the main reflection. The position of sub-peaks can either be within the width or adjacent to the main reflection depending on the lattice parameter change. Residual stress in Ti-6Al-4V causes slight changes in the lattice parameters of the HCP crystal that are in the order of 0.01nm.⁸⁸ The latter slightly shifts the 2 theta position of residual stress sub-peaks within the width of the main HCP reflection.⁸⁸ A large lattice parameter change from 0.293nm (alpha) to 0.5793nm significantly shifts 2 theta, and positions Ti₃Al sub-peaks adjacent to the main HCP reflection. Consequently sub-peaks from Ti₃Al precipitates are adjacent to the main HCP reflection.

Alloyed hydrogen increases the full width at half maximum (FWHM): this expands XRD reflections and overshadows Ti₃Al sub-peaks. Therefore Ti₃Al precipitates could not be effectively identified from sub-peaks in hydrogenated Ti-6Al-4V. Consequently, SAD analysis was used to confirm Ti₃Al precipitates in hydrogenated Ti-6Al-4V. Sub-peaks were effectively used to identify Ti₃Al precipitates in dehydrogenated Ti-6Al-4V.

3.4.2 Complementary phase and composition mapping using EBSD, TKD and EDS

Phase evolution in hydrogen treated Ti-6Al-4V was mapped using electron backscatter diffraction (EBSD) and transmission Kikuchi diffraction (TKD). The EBSD and TKD analyses were performed in the JEOL SEM 7100F at the conditions stipulated in **Table 3.4**.

Table 3.4: EBSD and TKD scanning parameters.

Parameter	EBSD	TKD
Acceleration voltage (kV)	20	20
Aperture (μm)	50	50
Probe current (nA)	5.07	5.07
Specimen tilt angle	+70	+20
Magnification	x2000, x6000	X1000
Vacuum (mbar)	10^{-4}	10^{-4}
Step size (nm)	200	10-20
Sample thickness (nm)	-	100-120

The TKD and EBSD mapping was performed with complementary energy dispersive spectroscopy (EDS) mapping. This was done to highlight the Al rich clusters which could potentially stabilise Ti_3Al . The TKD optimised the spatial resolution of EBSD and provided high resolution information at a broader field of view. This provided evidence which supported the limited field of view in the information that was attained in subsequent high resolution TEM analysis.

The TKD/EDS couple identified Al enrichment within the HCP phase at a high spatial resolution. It identified Al rich clusters at high spatial resolution which strongly indicated Ti_3Al precipitation in the respective HCP grains. The degree of Al enrichment in the Al rich clusters and concomitant Ti_3Al precipitation was subsequently confirmed using EDS and selected area diffraction in the TEM.

3.4.3 Confirmation of Ti_3Al precipitates in Al enriched clusters

High resolution transmission electron microscopy (HRTEM) was performed in a LaB₆, 200kV, JEOL JEM2100 which was operated in TEM-microprobe, TEM-nanoprobe or Scanning TEM (STEM) modes.

The JEOL JEM 2100 has a TEM resolution of 0.19nm and was equipped with (HAADF and EDS) analytical detectors that enabled complementary dark field imaging and chemical analysis at nanometre resolution.

Atomic resolution HAADF STEM and EDS characterisation was performed on the field emission ARM 200F which has a TEM point resolution of 0.11nm and a STEM resolution of 0.07nm. High resolution and atomic resolution STEM was performed at 200 kV at the stipulated camera lengths:

- 8cm: [inner = 34mRad - outer = 138mRad (detector collection)]
- 5cm: [inner = 50mRad - outer = 201mRad (detector collection)].

High resolution and atomic resolution HAADF STEM imaging was performed to identify aluminium or vanadium enriched areas in electron transparent TEM samples. The HAADF STEM imaging was performed with complementary EDS to support the composition variations highlighted by the atomic Z-contrast in HAADF STEM micrographs. Selected area diffraction was subsequently performed in Al enriched areas to confirm Ti_3Al precipitates.

The Gatan Digital Micrograph™ software was used to post process TEM micrographs. This primarily included measuring d-spacings in selected area diffraction patterns and processing fast Fourier transforms.

The crystal structure was confirmed by comparing the d-spacings in experimentally attained SAD patterns or reduced fast Fourier transforms (FFT) to referenced standards which were modelled in the Java Electron Microscopy Software (JEMS).

3.5 Sample preparation

This section documents the procedures that were performed to prepare samples for characterisation using the techniques outlined in **Section 3.4**.

3.5.1 EBSD and XRD analysis sample preparation

Bulk EBSD and XRD samples were mechanically ground and polished to a 0.05 μm micron oxide finish for EBSD analysis. The detailed mechanical polishing procedure is outlined in **Table 3.5**. A Struers MD Dur silk cloth was used for fine grinding to a 6 μm and 3 μm finish because it offers a high degree of planeness. The Struers MD Chem neoprene cloth was used for the final polishing of EBSD samples using an attack solution which consists of a 1:5 ratio of 40% hydrogen peroxide (H_2O_2) and 0.05 μm oxide polishing solution.

Table 3.5: Mechanical polishing procedure for EBSD analysis.

Solution (μm)	Polishing cloth	Time (min)	Load (N)	Speed (RPM)
6	Struers MD Dur	10	20	150
3				
1	Struers MD Chem			
0.25				
0.05 and H ₂ O ₂ attack				

3.5.2 Electron transparent 3mm diameter disk preparation

Bulk Ti-6Al-4V samples were ground to 200 μm thickness and 3mm disks were mechanically punched from non-hydrogenated samples. The brittle (hydrogenated) Ti-6Al-4V samples underwent brittle failure during disk punching. Therefore they were electric discharge machined (EDM) or spark eroded using a hollow 3mm diameter copper electrode and deionised water as a dielectric. Extracted 3mm diameter disks were subsequently ground to 100 μm thickness to eliminate the plastic deformation or the damage layer from EDM machining.

The 100 μm thick disks were either dimple ground and precision ion polished to electron transparency or jet polished to avoid ion milling induced damage. The dimpled disks were

ground to a 30µm dimple thickness on the Gatan Dimple Grider™ using a 6µm lubricant and a 20g load. An electron transparent region was subsequently precision ion milled in the Gatan precision ion polishing system (PIPS). Ion milling was performed at 5KeV, at a gun angle of 5° and a rotation speed of 3rpm. Alternatively, 100 µm thick disks were twin jet polished to electron transparency using a Struers Tenupol-5 twin-jet electropolisher and an electrolyte solution consisting of 60ml perchloric acid, 350ml butanol and 590ml methanol. The voltage was kept at 15V and the temperature was kept at -30°C.

3.5.3 Site specific electron transparent FIB-SEM foil preparation

Site specific samples were extracted using a focused ion beam (FIB) in the FEI Helios NanoLab DualBeam 650 scanning electron microscope (SEM). **Figure 3.6 a-d)** illustrates the site specific sample extraction in the Helios NanoLab DualBeam 650.

The sample was concentrically aligned to the electron and ion beams and kept at eucentric height to ensure that its focus and field of view remain constant during tilting. A protective carbon layer of approximate dimensions 10x2x2 µm length, width, depth was deposited on the site of interest (SOI) at a sample angle of 0° as shown in **Figure 3.6 a)**.

The sample was then tilted by 52° to excavate trenches around the SOI. Trenches of approximate dimensions 22x6x6 µm length, width, depth were excavated along the length of the carbon layer (see **Figure 3.6 b)**, using Ga ions at a current of 46nA. The current was subsequently reduced to 9nA to mill off the Ga ion damage on the sample, this was done by altering the tilt angle between 49° and 55°.

The sample was then extracted in four consecutive stages: L-shaped undercut, Omniprobe Autoprobe™ attachment, sample detachment and sample lift-out. An L shaped undercut was made to partially detach the sample. The partially detached sample was attached to the Omniprobe Autoprobe™ by depositing a carbon layer at the intersection of the probe and the sample. The sample was then fully detached by extending the L-shaped undercut to a U-shaped undercut as shown in **Figure 3.6 c)** and retracted using the Omniprobe Autoprobe™. At a 0° tilt, a 60° stage rotation, positioned a copper (Cu) grid at concentric and eucentric height. The Omniprobe Autoprobe™ (with attached sample) was re-inserted to eucentric

height in order to carbon mount the sample onto the Cu grid, and subsequently detach the probe.

The mounted sample was subsequently thinned to electron transparency. At a voltage and current of 30kV and 781Pa, Ga ions were used to initially thin opposite planes of the sample by tilting between 50° and 53° as shown in **Figure 3.6 d)**. The voltage and current was progressively reduced during milling up to the 5kV, 3.2nA settings that were used for final milling of the 100nm thick electron transparent sample.

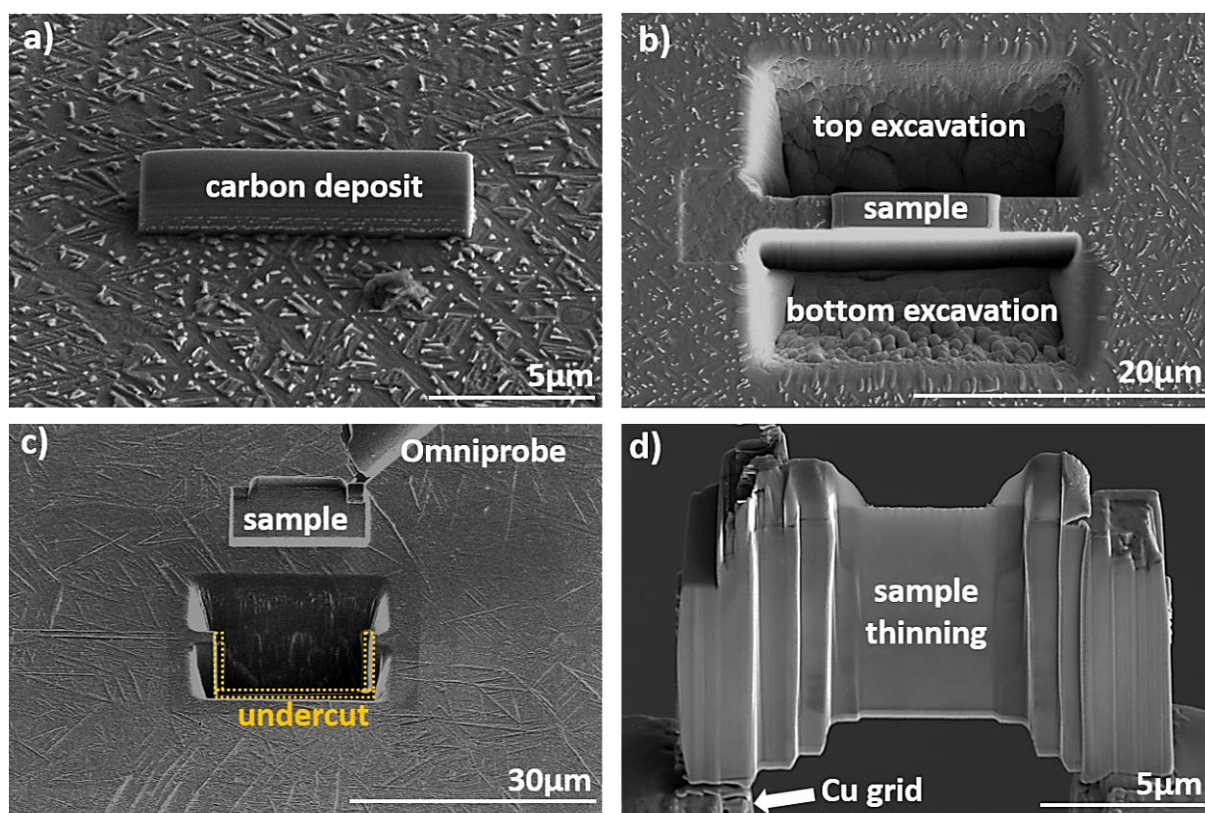


Figure 3.6: An illustrated site specific sample extraction procedure in the Helios NanoLab DualBeam 650. In a) a protective carbon layer was deposited to protect the sample during subsequent b) trenching. The sample was then c) detached by undercutting and subsequently attached to an Omniprobe. The detached sample was then d) attached to a Cu grid and thinned to electron transparency.

CHAPTER 4: THE HYDROGENATED Ti-6Al-4V MICROSTRUCTURE

This chapter investigates the effect of 20 at.% alloyed hydrogen on the Ti-6Al-4V microstructure. It also investigates the extent to which the hydrogenated microstructure reflects hydrogenation-disproportionation.

Simulated cast (Sim. cast) Ti-6Al-4V rods were hydrogenated to 20 at.%H by annealing in a positive hydrogen atmosphere for 12 hours at 650°C. The control treatment, annealed simulated cast (A. Sim. cast) was prepared by annealing at 650°C for 12 hours in a vacuum atmosphere. Sections were extracted from the rods for microstructure characterisation using: X-ray diffraction (XRD), electron backscatter diffraction (EBSD), energy dispersive spectroscopy (EDS), transmission Kikuchi diffraction (TKD), high angle annular dark field STEM (HAADF STEM) and selected area diffraction (SAD).

Chapter 4 presents the microstructure, phase constitution and phase composition of non-hydrogenated Ti-6Al-4V and subsequently compares the latter to hydrogenated Ti-6Al-4V. It confirms hydride precipitates in hydrogenated Ti-6Al-4V and landmarks them as vanadium rich and aluminium lean. This landmark was used to trace the effect of hydride precipitates on surrounding microstructure regions. Land marking hydride regions was convenient in instances where vacuum exposure inadvertently dehydrogenated electron transparent samples and decomposed hydrides during TKD or TEM analysis.

Chapter 4 concludes that the hydrogenated Ti-6Al-4V microstructure has elements of hydrogenation-disproportionation. This is because hydrogenation transformed lamellae alpha into distinct Al rich and V rich regions. The Al rich regions stabilised Ti_3Al and the V rich regions ultimately stabilised beta (after dehydrogenation - see **Chapter 5**). This occurred through a hydride induced partitioning or rejection of aluminium. Alloyed hydrogen (20 at.%) precipitated Ti-H or Ti-H₂ hydrides which partitioned aluminium from its Ti-Al couple. The partitioned aluminium concentrated in neighbouring microstructure regions to form Al rich clusters, where the Al enrichment exceeded the critical Al content that stabilised Ti_3Al precipitates. However, disproportionation did not proceed through the rejection or partitioning of vanadium from hydrides (as proposed in literature). Instead, hydrides retained their characteristic vanadium enrichment.

4.1 Non-hydrogenated Ti-6Al-4V

Section 4.1 presents the morphology, phase constitution and phase composition of non-hydrogenated Ti-6Al-4V. Non-hydrogenated Ti-6Al-4V includes simulated cast (Sim. cast) and annealed simulated cast (A. Sim. cast) Ti-6Al-4V.

4.1.1 Morphology and phase constitution of non-hydrogenated Ti-6Al-4V

Figures 4.1 and **4.2** present EBSD phase maps of simulated cast (**Figure 4.1**) and annealed simulated cast (**Figure 4.2**) Ti-6Al-4V. Annealing simulated cast Ti-6Al-4V at 650°C for 12 hours in the absence of hydrogen does not precipitate hydrides. This is because the EBSD phase maps of simulated cast Ti-6Al-4V and its annealed counterpart only confirm equilibrium alpha (HCP), retained beta (BCC) and no hydride phase. Simulated cast Ti-6Al-4V and its annealed counterpart have a Widmanstätten morphology consisting of retained beta interlamellae and HCP lamellae regions. **Figure 4.3 a-c)** shows complementary backscatter and EDS analysis highlighting the aluminium and vanadium distribution in the Widmanstätten microstructure. Atomic Z-contrast in **Figure 4.3 a)** highlights the vanadium (V) rich, retained beta interlamellae regions in bright contrast and the aluminium (Al) rich lamellae regions in dark contrast. The EDS maps in **Figure 4.3 b-c)** reiterate the V and Al enrichment at the interlamellae and lamellae regions respectively. Cross-referencing **Figure 4.3** with **Figures 4.1-4.2** confirms that the V rich interlamellae are BCC beta phase and the Al rich lamellae are HCP alpha phase. **Figures 4.1-4.3** show that non-hydrogenated Ti-6Al-4V has a Widmanstätten morphology of alpha and retained beta phases which are typically enriched in Al, V respectively.

4.1.2 Expected degree of Al partitioning and enrichment in non-hydrogenated Ti-6Al-4V

Figure 4.4 quantifies the expected degree of Al partitioning between alpha and beta phases in non-hydrogenated Ti-6Al-4V (Sim. cast and A. Sim. Cast). It shows that the expected degree of Al partitioning is up to approximately 4 at.%Al in beta and 12 at.%Al in alpha. This degree of Al partitioning is expected because the Ti-6Al-4V stoichiometric ratio in atomic percent is approximately Ti-10.2Al-3.6V. In summary, there is no significant difference in the morphology, phase constitution and the composition of non-hydrogenated Ti-6Al-4V. Therefore any significant phase or composition variation from **Figures 4.1-4.4** that will be observed in the hydrogenated Ti-6Al-4V microstructure is caused by the alloyed hydrogen.

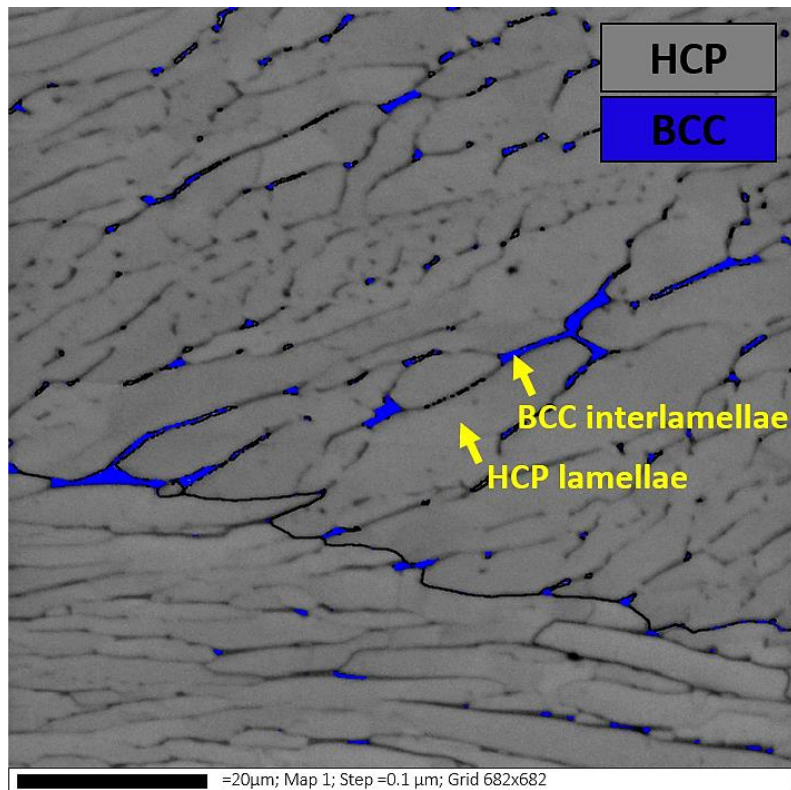


Figure 4. 1: a) EBSD phase map of simulated cast (Sim. cast) Ti-6Al-4V showing Widmanstätten beta (BCC-blue) interlamellae and alpha (HCP-grey) lamellae regions.

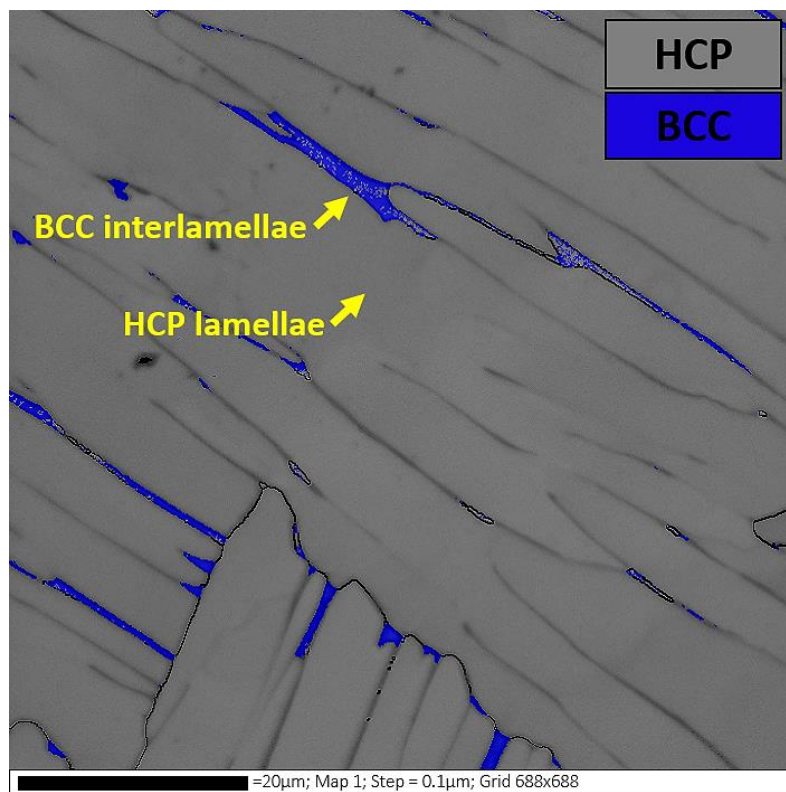


Figure 4. 2: a) EBSD phase map of annealed simulated cast (A. Sim. cast) Ti-6Al-4V showing Widmanstätten beta (BCC-blue) interlamellae and alpha (HCP-grey) lamellae regions. Annealing simulated cast Ti-6Al-4V at 650°C for 12 hours in the absence of hydrogen does not precipitate hydrides.

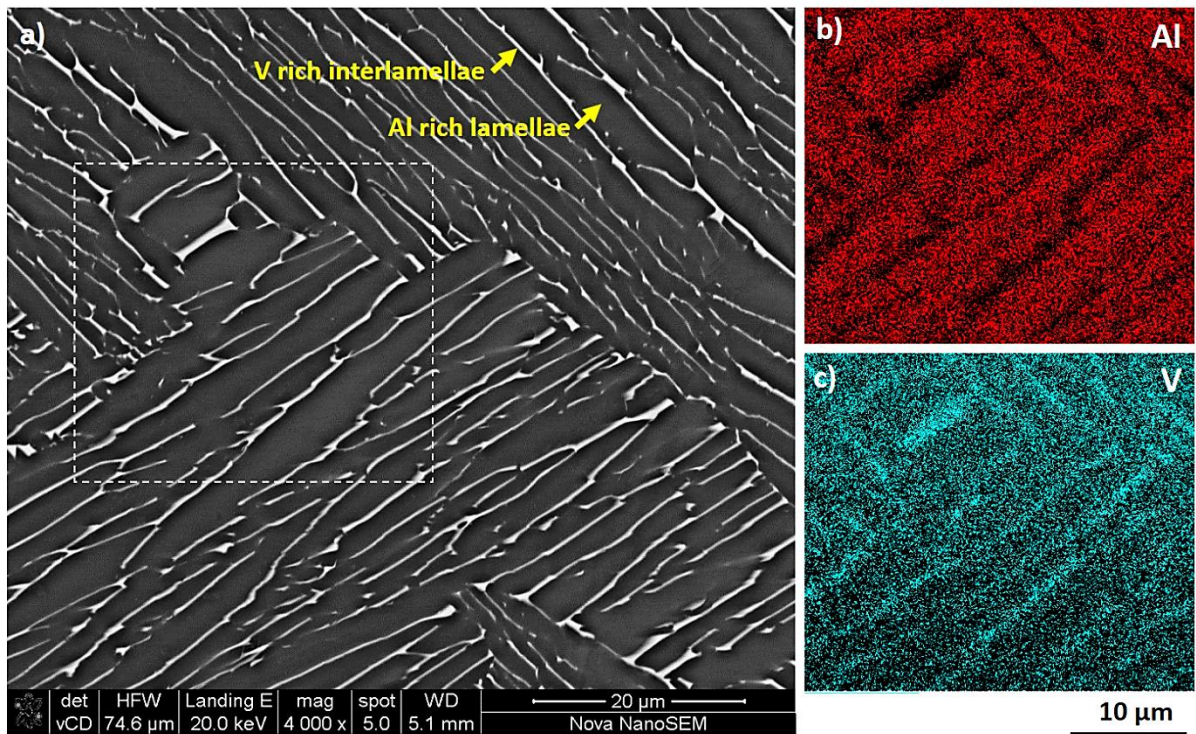


Figure 4. 3: Simulated cast Ti-6Al-4V a) backscattered electron and EDS maps of b) Al and c) V attained from the highlighted area in a). The atomic Z-contrast in image a) highlights V rich interlamellae in bright contrast and an Al rich lamellae region in dark contrast. The EDS maps in b) and c) reiterate the Al enrichment in the lamellae region and the V enrichment in the interlamellae region.

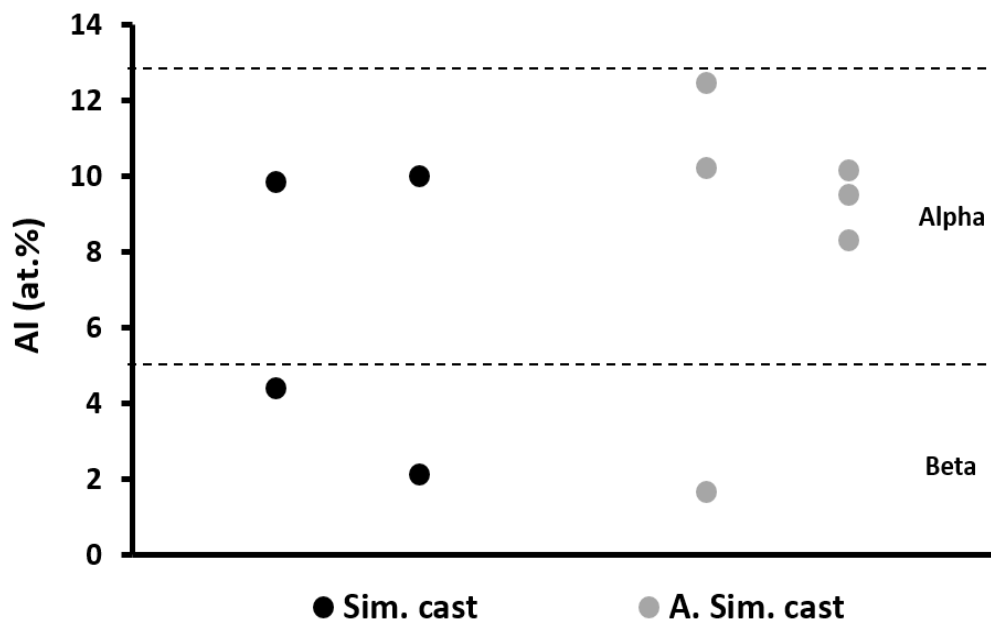


Figure 4. 4: EDS point analysis showing the degree of Al enrichment in non-hydrogenated Ti-6Al-4V which comprises of simulated cast (Sim. cast) and annealed simulated cast (A. Sim. cast). The degree of Al enrichment in non-hydrogenated Ti-6Al-4V is up to 12 at.%Al.

4.2 Bulk phase comparison in hydrogenated and non-hydrogenated Ti-6Al-4V

Section 4.2 compares the bulk phase constitution in non-hydrogenated and 20 at.% hydrogenated Ti-6Al-4V using XRD analysis. **Figure 4.5 a, b)** compares the XRD patterns of simulated cast (Sim. cast) and 20 at.% hydrogenated Ti-6Al-4V (H).

4.2.1 Equilibrium phases (alpha and beta)

The room temperature volume fractions of alpha and beta phases in non-hydrogenated Ti-6Al-4V are approximately 90% and 10%.⁵⁶ Therefore the simulated cast patterns in **Figure 4.5 a, b)**, mostly has HCP peaks and only two BCC peaks which are β_{110} at 39.5° and β_{220} at 85° .

Comparatively, hydrogenated Ti-6Al-4V has additional beta peaks, β_{200} at 55° and β_{211} at 69° because of the beta stabilising effect of hydrogen. The lattice expansion from hydrogen alloying reduced the Bragg diffraction angle and shifted peaks to lower 2 theta positions, where they occasionally merged with other diffraction peaks. The hydrogenated Ti-6Al-4V spectra shows that β_{110} at 39.5° shifted and merged with α_{0002} at 38.5° , the alpha peaks between 75° and 80° ($\alpha_{20\bar{2}0}, \alpha_{11\bar{2}2}, \alpha_{20\bar{2}1}$) merged and the β_{220} shifted from 85° to 82° .

4.2.2 Hydrogen induced phases (Hydride and Ti_3Al)

Figure 4.5 a, b), shows delta hydride reflections $\delta_{111}, \delta_{200}, \delta_{202}, \delta_{220}, \delta_{222}$ at 2 theta $35.5^\circ, 40.5^\circ, 60^\circ, 62^\circ$ and 73° respectively. Most of the hydride reflections overlap with alpha reflections and can be confused with hydrogen saturated alpha. However, the non-overlapping δ_{202} reflection at 2 theta 60° unambiguously confirms that hydride precipitates are present in Ti-6Al-4V hydrogenated to 20 at.% hydrogen.

Alpha and Ti_3Al have the same crystal structure (HCP), and c-lattice parameters but they have different a -lattice parameters of 0.5793nm (Ti_3Al) and 0.293nm (alpha).⁸¹ The a -lattice parameter difference manifests as sub-peaks on main HCP reflections. There are no sub-peaks in non-hydrogenated Ti-6Al-4V, which means there is no depicted variation in alpha lattice parameters from Ti_3Al superlattice formation. The Ti_3Al sub-peaks are expected in hydrogenated Ti-6Al-4V. However, they are also not observed because they are overshadowed by peak broadening.

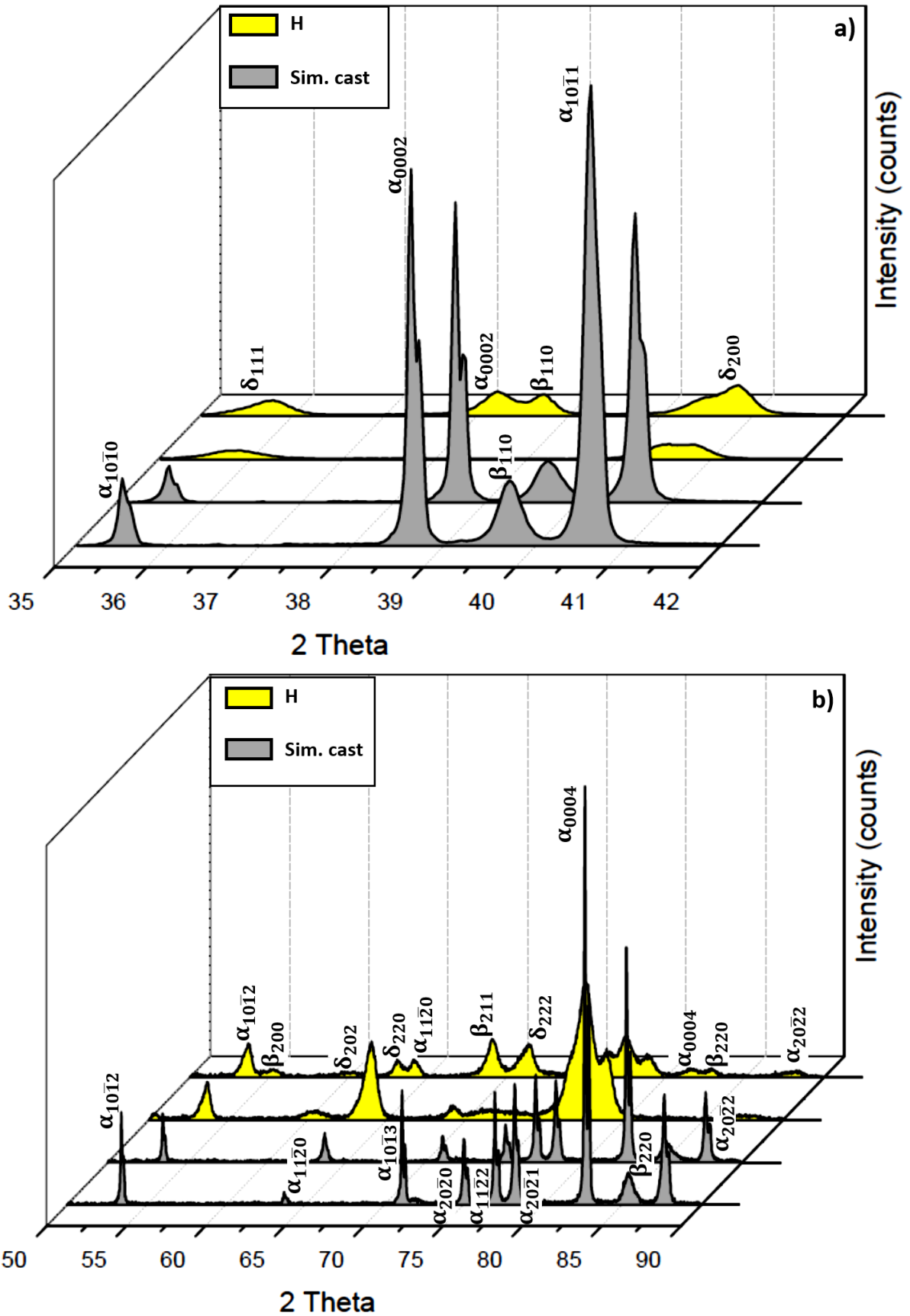


Figure 4. 5: XRD patterns of simulated cast (Sim. cast) and hydrogenated (H) Ti-6Al-4V at 2 theta a) 35°-42° and b) 50°-90°. Non-hydrogenated Ti-6Al-4V (Sim. cast) has alpha (α) and beta (β) phases whilst hydrogenated Ti-6Al-4V has additional beta phase and hydrides.

4.3 Ti-6Al-4V microstructure evolution during hydrogenation

The phase constitution and composition in 20 at.% hydrogenated Ti-6Al-4V was mapped using complementary electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS).

Figures 4.6 a-c) and **4.7 a-c)** are complementary EBSD phase and EDS maps of hydrogenated Ti-6Al-4V. They show that hydrogenated Ti-6Al-4V has alpha (HCP), beta (BCC), face centered cubic (FCC) hydride and face centered tetragonal (FCT) hydride phases. The morphology of the hydrogenated microstructure is similar to the simulated cast microstructure; they both have V rich interlamellae and an Al rich lamellae region. However, the V rich interlamellae in hydrogenated Ti-6Al-4V are predominantly FCC or FCT hydride precipitates instead of BCC phase. In addition, the lamellae region in hydrogenated Ti-6Al-4V is predominantly (not fully) Al rich because it also has fine V rich precipitates. Hydride phase precipitated in the interlamellae region as hydride laths and in the lamellae region as fine hydride precipitates. The lath hydrides and the fine hydride precipitates were all enriched in vanadium.

4.3.1 Annealing for 12 hours at 650°C

The volume fraction of BCC phase in non-hydrogenated Ti-6Al-4V increases from 10% to 20% between 800°C and 850°C⁸⁹ and non-hydrogenated Ti-6Al-4V becomes fully BCC above 1050°C.⁴² Therefore at 650°C, non-hydrogenated Ti-6Al-4V has 10% BCC phase.⁸⁹

Reports of hydrogenated Ti-6Al-4V in the open literature have not quantified the subtransus volume fractions of BCC phase. Notwithstanding this, it is rational to think that hydrogenated Ti-6Al-4V had a comparatively higher BCC volume fraction at 650°C. This is because the hydrogenated Ti-6Al-4V spectra (in **Figure 4.5**) has additional BCC peaks, β_{200} at 55° and β_{211} at 69° that are not observed in non-hydrogenated Ti-6Al-4V. The additional BCC peaks result from the beta stabilising effect of the 20 at.% alloyed hydrogen which has been shown to decrease the beta transus temperature from 1050°C to 800°C.⁴² The lower beta transus stabilises a higher volume fraction of BCC phase at lower annealing temperatures.

The higher volume fraction of BCC phase in the hydrogenated sample can also be traced from its vanadium rich regions. Before hydrogenation, extensive vanadium enrichment was only observed in the BCC interlamellae region (**Figures 4.1 and 4.3**). After hydrogenation, extensive vanadium enrichment is also observed in the lamellae region where it manifests as fine and vanadium rich hydride precipitates (**Figures 4.6 and 4.7**). The higher volume fraction of hydrogen stabilised BCC phase consequently reduced the HCP volume fraction at 650°C. This intensified Al partitioning towards the “hydrogen reduced” HCP volume fraction.

4.3.2 Furnace cooling from 650°C to room temperature

Slow cooling hydrogenated Ti-6Al-4V from 650°C transformed the hydrogen stabilised BCC phase to HCP phase. The BCC phase dissolves more hydrogen (up to 45 at.%H)^{43, 51} when compared to HCP phase which dissolves up to 8 at.%H.^{8, 43} Hydrides can directly precipitate in BCC phase when the hydrogen content exceeds 45 at.%H.⁴³ However, the lack of high hydrogen bearing FCT-ε hydrides ($c/a < 1$)⁵¹ in the hydrogenated microstructure (**Figures 4.6 and 4.7**) suggests that a direct BCC to hydride transformation was unlikely to occur. Instead, the hydrogenated microstructure has a small fraction of low hydrogen bearing FCT-γ (or Ti-H) hydride ($c/a > 1$), and a large fraction of medium hydrogen bearing FCC-δ (or Ti-H₂) hydrides which precipitate at a Ti-H_x composition range of ($1.5 < x < 2$).⁷⁶ Therefore, the BCC phase most likely transformed to hydrogen saturated HCP phase and ultimately FCC or FCT hydride during cooling. The HCP to FCC transformation would also be favoured over a direct BCC to FCC transformation because it has a 5% volume misfit whilst the direct transformation has a 14% volume misfit.⁹⁰⁻⁹²

The Ti-H₂ (FCC) and Ti-H (FCT) hydride phases precipitated as hydride laths (in the interlamellae region) and as fine hydride precipitates (in the lamellae region). The hydride precipitates were rich in vanadium because they retained the parent BCC grain composition which is characteristically rich in vanadium. This means that the composition of the decomposing BCC volume was not significantly altered during the BCC, hydrogen saturated HCP and ultimately FCC or FCT hydride transformation. This is expected because the diffusivity of Al and V at 900°C (10^{-14} m²/s) is significantly lower than that of hydrogen at 650°C (10^{-9} m²/s) as shown in **Figure 2.11**.^{50, 75, 76} The effect of hydrides on the microstructure is presented in **Section 4.4**.

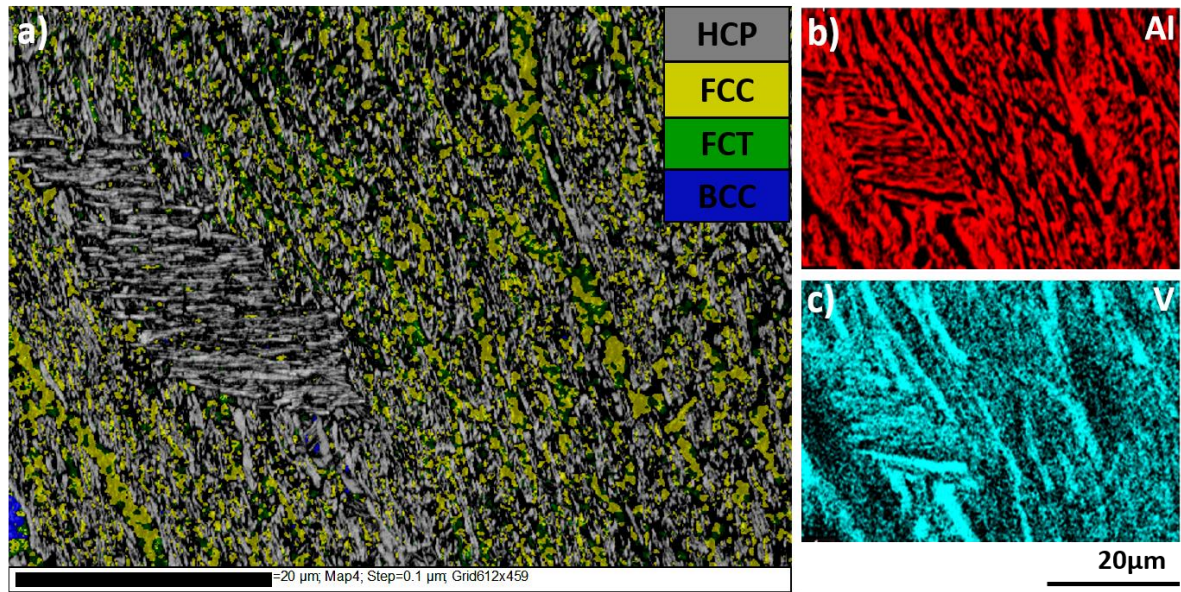


Figure 4. 6: a) Complementary EBSD phase and b, c) EDS maps of hydrogenated Ti-6Al-4V. Image a) is colour coded to show; grey (HCP), blue (BCC), yellow (FCC or Ti-H₂), and green (FCT or Ti-H) phases which correspond to alpha, beta, delta (δ) hydride and γ hydride respectively. Images b, c) show that the FCC, FCT hydrides are rich in V and depleted in Al.

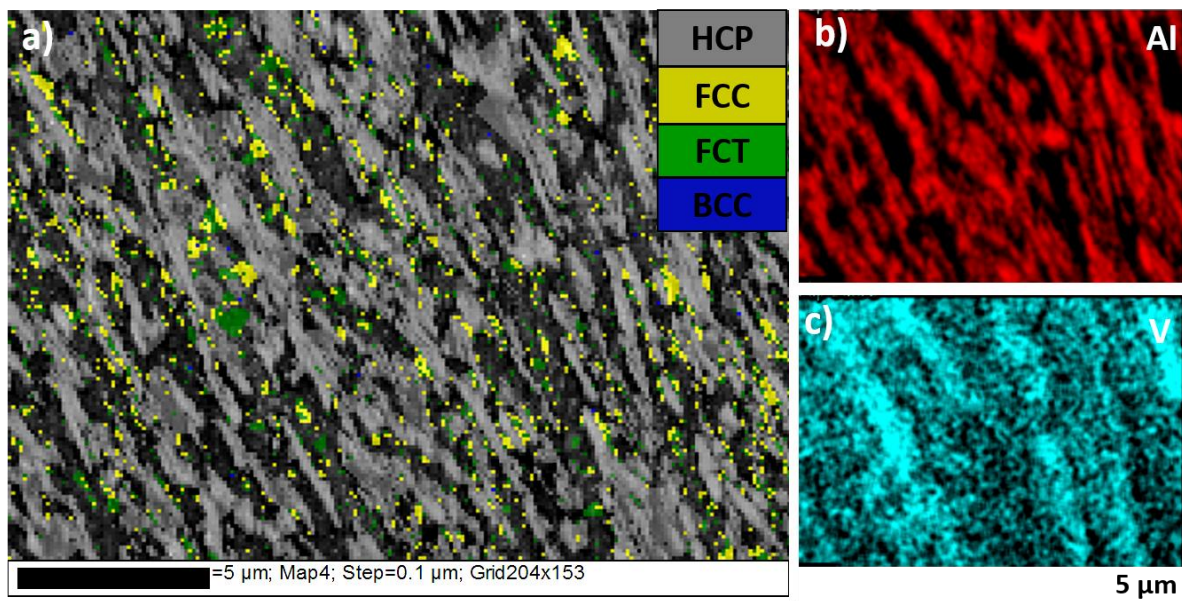


Figure 4. 7: a) High magnification EBSD phase and b, c) EDS maps of hydride laths in hydrogenated Ti-6Al-4V. Image a) is colour coded to show; grey (HCP), blue (BCC), yellow (FCC or Ti-H₂), and green (FCT or Ti-H) phases which correspond to alpha, beta, delta (δ) hydride and γ hydride respectively. Images b, c) show that the FCC, FCT hydride laths are rich in V and depleted in Al.

4.4 The effect of hydrides on Al and V partitioning

The effect of hydride precipitates on the microstructure was characterised from electron transparent foils which were extracted from hydride laths and fine hydride precipitates.

4.4.1 Hydride extraction

Figures 4.6 and 4.7 confirmed that hydride phase precipitates as hydride laths (in the interlamellae region) and fine hydride precipitates (in the lamellae region). The hydride laths and the fine hydride precipitates are both enriched in vanadium (V). Electron transparent foils were extracted from hydride laths and fine hydride precipitates using a focused ion beam (FIB) in the scanning electron microscope (SEM). Backscatter imaging highlighted the regions of interest during extraction. **Figure 4.8 a, b)** is a backscattered electron micrograph of hydrogenated Ti-6Al-4V showing V rich interlamellae (bright contrast) and the lamellae region (dark contrast). Electron transparent FIB-SEM foils encompassing hydride precipitates were extracted from V rich interlamellae and fine V rich precipitates. This is illustrated in **Figure 4.8 b)** where FIB-SEM foils 1 and 2 were extracted from V rich interlamellae and FIB-SEM foil 3 was extracted from fine V rich precipitates in the lamellae region.

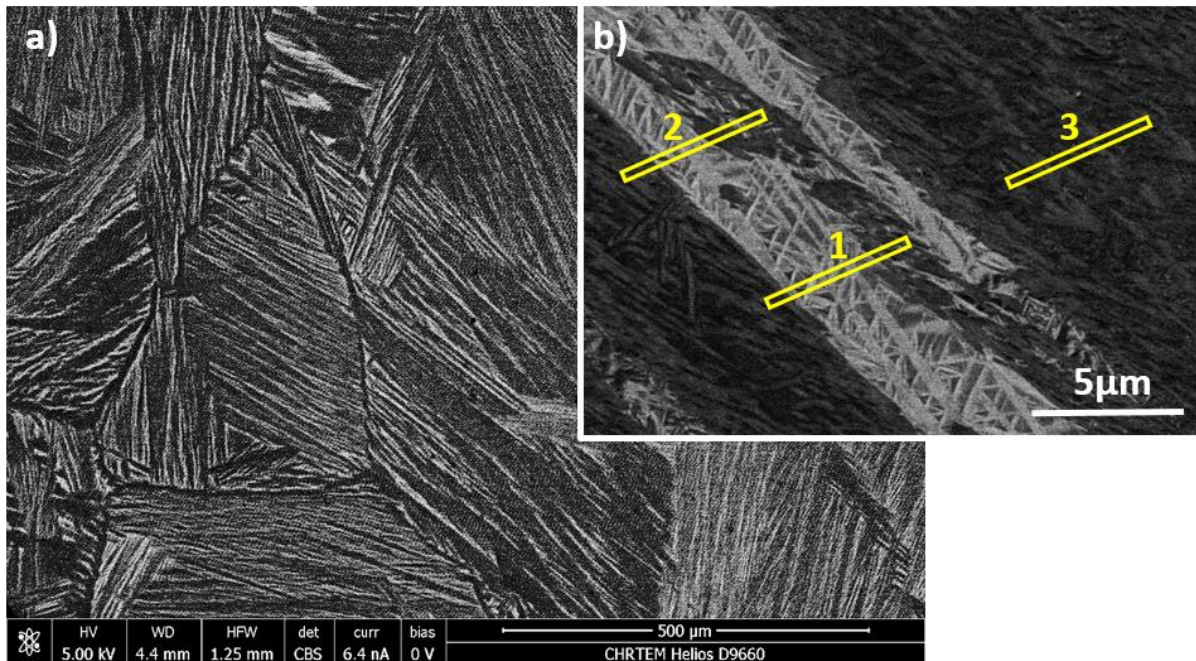


Figure 4. 8: a, b) Backscattered electron micrographs of hydrogenated Ti-6Al-4V highlighting vanadium (V) rich interlamellae (bright) and the predominantly aluminium (Al) rich lamellae region (dark). Image b) illustrates the extraction sites for FIB-SEM foils, where 1 and 2 encompass V rich hydride laths and 3 encompasses fine V rich hydride precipitates.

4.4.2 Partitioning at hydride laths

Electron transparent FIB-SEM foils 1 and 2 were extracted from V rich hydride laths (**Figure 4.8 b1 and b2**). They were subsequently analysed using high angle annular dark field (HAADF), transmission Kikuchi diffraction (TKD) and energy dispersive spectroscopy (EDS). **Figures 4.9 a-d)** and **4.10 a-d)** present a) HAADF STEM b) TKD and EDS c) Al, d) V analyses of the hydride laths. The analysed area is highlighted in white in **Figures 4.9 a)** and **4.10 a)**. The atomic Z-contrast in **Figures 4.9 a)** and **4.10 a)** highlights V, Al enrichment in bright, dark contrasts respectively. It is complemented by the EDS maps in **Figures 4.9 c, d)** and **4.10 c, d)** which confirm the V, Al enrichment in the analysed area. **Figures 4.9 d)** and **4.10 d)** show that the V rich hydride laths are successfully captured in the field of view of electron transparent FIB-SEM foils 1 and 2.

However, the TKD phase maps in **Figures 4.9 b)** and **4.10 b)** do not confirm any hydride phase in FIB-SEM foils 1 and 2. Instead, they expectedly confirm Al rich regions as HCP phase and unexpectedly confirm V rich regions also as HCP phase. The unexpected confirmation of V rich regions as HCP phase reveals a disconnect between the EBSD phase analysis on the bulk sample and the TKD phase analysis on the electron transparent foils 1 and 2. This means that dissolved hydrogen inadvertently escaped from electron transparent FIB-SEM foils 1 and 2 after they were exposed to high vacuum in the microscope. The inadvertent escape could not be quantitatively validated in the TEM because it is impossible to elementally map hydrogen. Inadvertent hydrogen escape can occur during foil extraction or during TKD or TEM analysis. Inadvertent hydrogen escape has also been reported to occur when ion milling electron transparent Nd-Fe-B samples.⁵⁴ Moreover, Bhosle et al.⁹³ also shows evidence of a room temperature FCC (TiH₂) hydride to HCP (alpha) decomposition after TiH₂ was exposed to the electron beam and a high vacuum in the TEM.

Hydrides precipitate to accommodate the lattice distortion that is caused by hydrogen saturation in the HCP crystal.⁵¹ Inadvertent hydrogen escape eliminated this distortion and made it possible for the HCP crystal to retain its symmetry. Therefore a room temperature TiH₂ hydride to HCP alpha transformation occurred.^{51, 94} The latter TiH₂ transformation was possible because hydrogen inserts at octahedral sites without altering the arrangement of titanium atoms.⁸⁰ A room temperature transformation that is driven by hydrogen escape has

limited kinetics to support Al and V diffusion. This is because the diffusivity of Al and V is substantially lower than the diffusivity of hydrogen (see **Section 2.10.1**). Consequently, the inadvertent hydride decomposition did not alter the elemental composition. This is evident in the V rich HCP phase that is indexed by TKD and EDS in **Figures 4.9-4.10**.

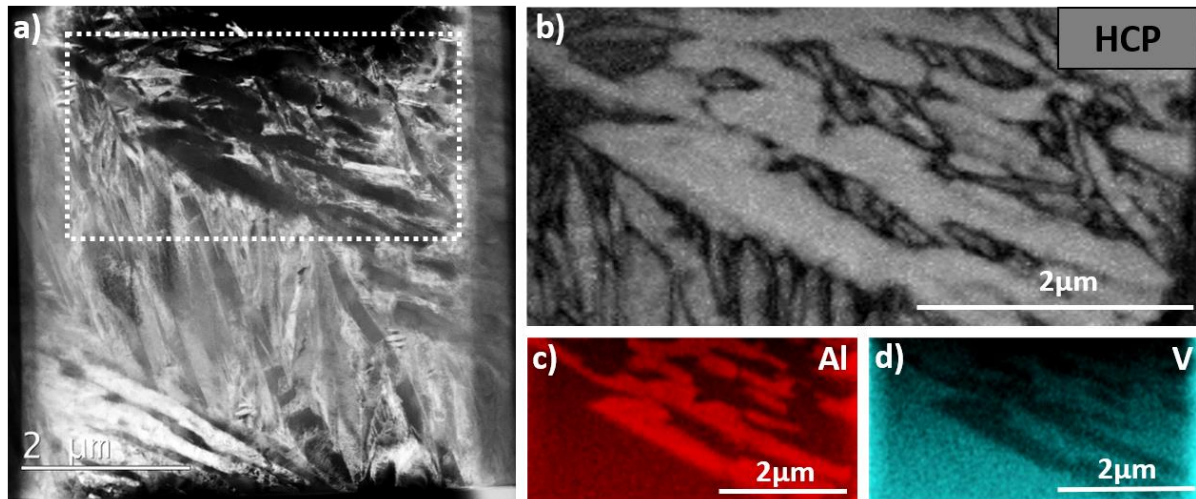


Figure 4. 9: FIB-SEM foil 1 showing a) HAADF STEM micrograph of 20 at.% hydrogenated Ti-6Al-4V showing the analysed area in white. Images b-d) are corresponding b) TKD phase map and EDS c) Al and d) V maps from the analysed area. Atomic Z-contrast in a) identifies V, Al rich regions in bright, dark contrast respectively. The TKD phase analysis in b) does not confirm hydrides, instead it confirms the Al rich and V rich regions as HCP (grey) phase.

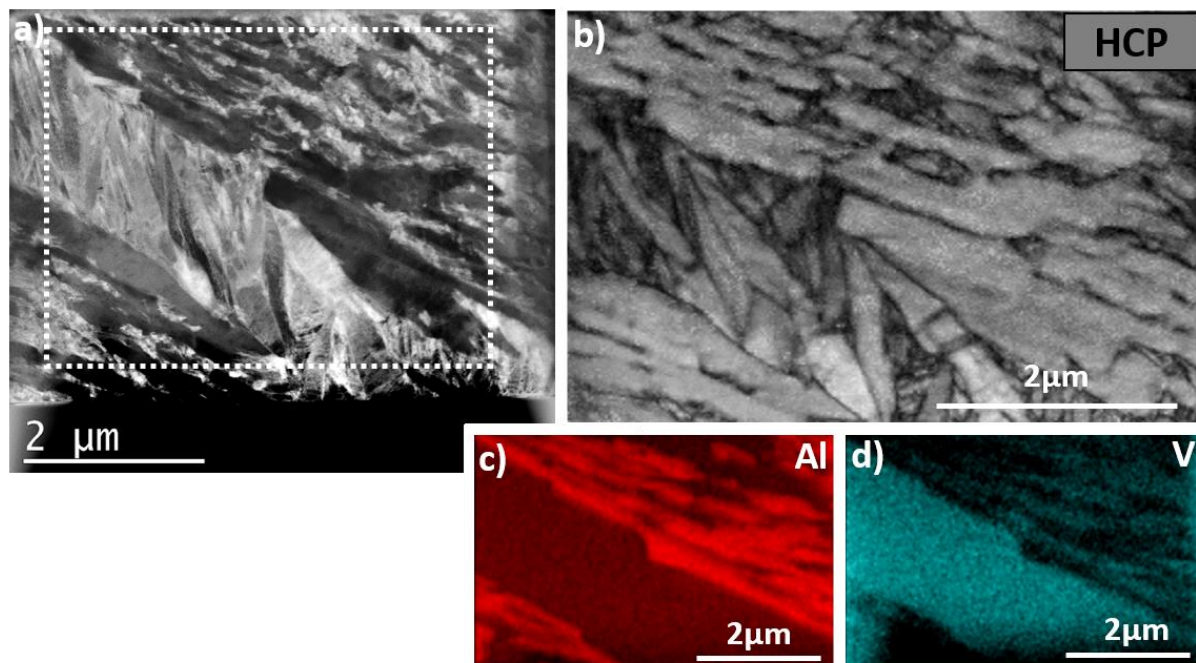


Figure 4. 10: FIB-SEM foil 2 showing a) HAADF STEM micrograph of 20 at.% hydrogenated Ti-6Al-4V showing the analysed area in white. Images b-d) are corresponding b) TKD phase map and EDS c) Al and d) V maps from the analysed area. Atomic Z-contrast in a) highlights V, Al rich regions in bright, dark contrast respectively. The TKD phase analysis in b) does not confirm hydrides, instead it confirms the Al rich and V rich regions as HCP (grey) phase.

The inadvertent hydrogen escape and the consequent transformation of hydrides to alpha was unexpected. However, it did not deter a post hydride decomposition analysis of the effect of hydride precipitates on the microstructure. The post hydride decomposition analysis was possible because the inadvertent hydride transformation occurred at room temperature and it did not affect the elemental composition. Therefore, it retained the characteristic V rich regions which identified prior hydride precipitates as hydride landmarks. More importantly, it also retained the hydride induced partitioning and clustering of aluminium in the microstructure.

4.4.3 The degree of Al enrichment in hydride partitioned Ti-6Al-4V

Figure 4.11 shows the degree of Al enrichment in 20 at.% hydrogenated Ti-6Al-4V and compares it to non-hydrogenated Ti-6Al-4V. The degree of Al enrichment as a result of Al partitioning in non-hydrogenated Ti-6Al-4V [simulated cast (Sim. cast) and annealed simulated cast (A. Sim. Cast)] was presented in **Figure 4.4** and it has been included in **Figure 4.11** for comparison. **Figure 4.11**, shows that extent of Al enrichment in non-hydrogenated Ti-6Al-4V is up to 11 at.%Al. In comparison, the degree of Al enrichment in hydrogenated Ti-6Al-4V is up to 26 at.%Al. The extensive Al enrichment that is unique in hydrogenated Ti-6Al-4V formulates the basis of the argument that is presented in **Chapter 4**.

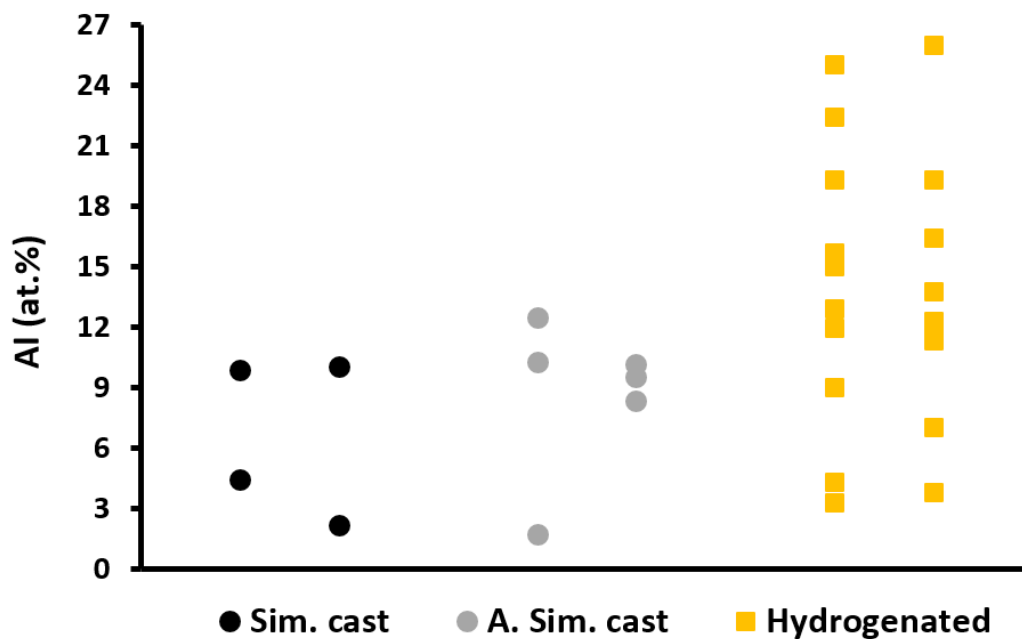


Figure 4. 11: The degree of aluminium enrichment in non-hydrogenated (Simulated cast -Sim. Cast and annealed simulated cast - A. Sim cast) and 20 at.%H hydrogenated Ti-6Al-4V. Alloyed hydrogen intensifies the degree of Al enrichment from a 12 at.%Al benchmark up to 26 at.%Al.

Alloyed hydrogen intensifies the degree of localised Al enrichment in the HCP phase in two ways:

- Firstly, hydrogen stabilises a greater volume fraction of sub-transus BCC phase (this is evidenced from the additional BCC peaks observed in the XRD spectra of hydrogenated Ti-6Al-4V, see **Section 4.2.1**). A greater volume of sub-transus BCC phase consequently decreases the sub-transus volume fraction of HCP phase. This increases Al partitioning towards the “hydrogen decreased” HCP volume fraction.
- Secondly, alloyed hydrogen stabilises FCT- γ (Ti-H) and FCC- δ (Ti-H₂) hydrides (see **Figures 4.6 and 4.7**). Hydrogen has a higher affinity for Ti when compared to Al,⁴³ therefore Ti-H and Ti-H₂ partition Al from its Ti-Al coupling. The partitioned Al concentrates in neighbouring regions to form Al rich clusters where the degree of Al enrichment can be up to 26 at.%Al (see **Figure 4.11**).

Figure 4.12 a-e) characterises the hydride partitioned microstructures in FIB-SEM foils 1 and 2. It maps the clustering of partitioned Al in regions neighbouring hydride landmarks. It also quantifies the degree of Al enrichment in the hydride landmarks and their neighbouring Al rich clusters. The dark atomic Z-contrast in **Figure 4.12 a, c)**, highlights the Al rich clusters in FIB-SEM foils 1 and 2. The Al enrichment at the clusters is reiterated by complementary EDS maps in **Figure 4.12 b, d)** and quantified by EDS point and region analysis in **Figure 4.12 e)**.

Figure 4.12 e) shows that the Al concentration ranges between 11-13 at.%Al in the hydride landmarks and 19-23 at.%Al in the neighbouring Al rich clusters. The maximum solubility of Al in alpha phase is predicted to be 10 at.%Al,⁸² therefore at least 11 at.%Al is required to initiate Ti₃Al precipitation in alpha phase.⁸³ Aluminium concentrations above the 11 at.%Al threshold are demonstrated to increase the size of Ti₃Al precipitates and the intensity of superlattice reflections.⁸³ The Al content at the hydride landmark regions (11-13 at.%Al) and their neighbouring Al rich clusters (19-23 at.%Al) meet the threshold Al content that initiates Ti₃Al precipitation. This alleges that Ti₃Al could precipitate at hydride landmark regions which have 11-13 at.%Al.⁸² Therefore selected area diffraction (SAD) was performed at the hydride landmark regions and the Al rich clusters of FIB-SEM foil 1 to confirm Ti₃Al precipitation.

The SAD analysis was performed at a region encompassing the Al rich cluster 2 (marked by EDS region 2) and the hydride landmark region 3 (marked by EDS region 3) in **Figure 4.12 b**). The SAD analysis is presented in **Figure 4.13** where the EDS regions 2, 3 correspond to R2, R3 respectively.

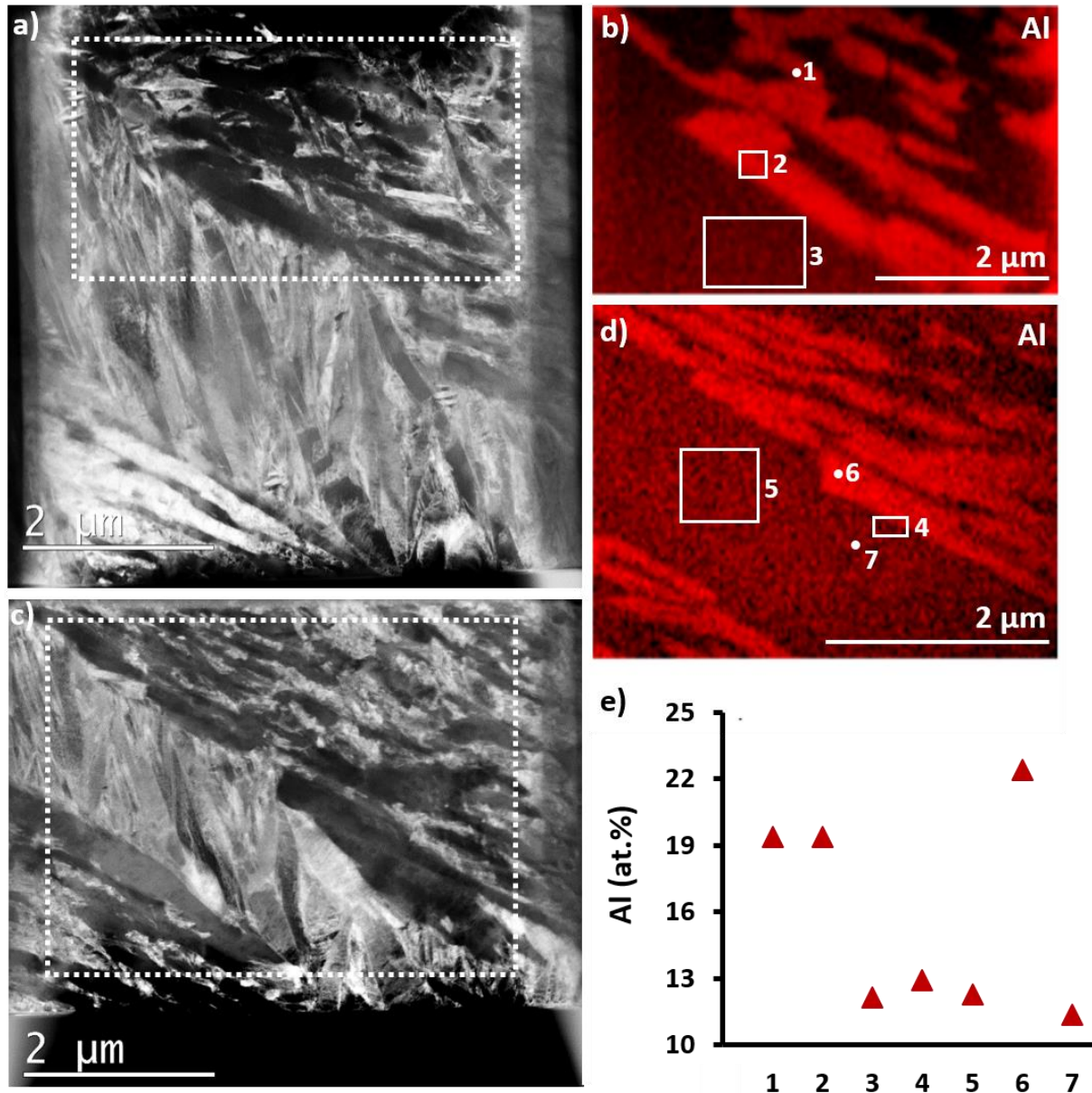


Figure 4. 12: a), c) HAADF STEM and b-e) EDS analyses of FIB-SEM foils a, b) 1 and c, d) 2 which were extracted from 20 at.%H hydrogenated Ti-6Al-4V. The complementary EDS maps b) and d) were mapped from the highlighted (in white) regions in a) and c) respectively. The EDS maps are marked with the EDS point and region analysis 1-7 that is presented in image e). Atomic Z-contrast in a) and c) highlights Al lean and Al rich regions in bright and dark contrasts respectively. The highlighted Al enrichment is reiterated in the complementary EDS maps in b) and d). Image e) quantifies the degree of Al enrichment to be up to 13 at.%Al in the Al lean regions (3,4,5,7) and up to 23 at.%Al in the Al rich regions (1,2,6).

Figure 4.13 a) shows a HAADF STEM micrograph of FIB-SEM foil 1 highlighting (in white circles) SAD analysed regions R1, R2 and R3. Atomic Z-contrast in a) shows that region R2 is Al rich whilst regions R1 and R3 are Al lean (V rich). The complementary SAD patterns confirm Ti_3Al phase at R2 and alpha phase at R1, R3 at the respective zone axes $[2\bar{1}\bar{1}3]$ Ti_3Al and $[10\bar{1}0]$, $[2\bar{1}\bar{1}3]$ alpha. The presence of superlattice reflections in the simulated $[10\bar{1}0]$ Ti_3Al diffraction pattern validates that the R3 zone axis $[10\bar{1}0]$ diffraction pattern is alpha and not Ti_3Al . The 13 at.%Al content in **Figure 4.12** (EDS region 3) did not stabilise Ti_3Al in **Figure 4.13** (R3). Therefore this study concludes that Al concentrations exceeding 13 at.%Al are required to stabilise Ti_3Al in 20 at.% hydrogenated Ti-6Al-4V.

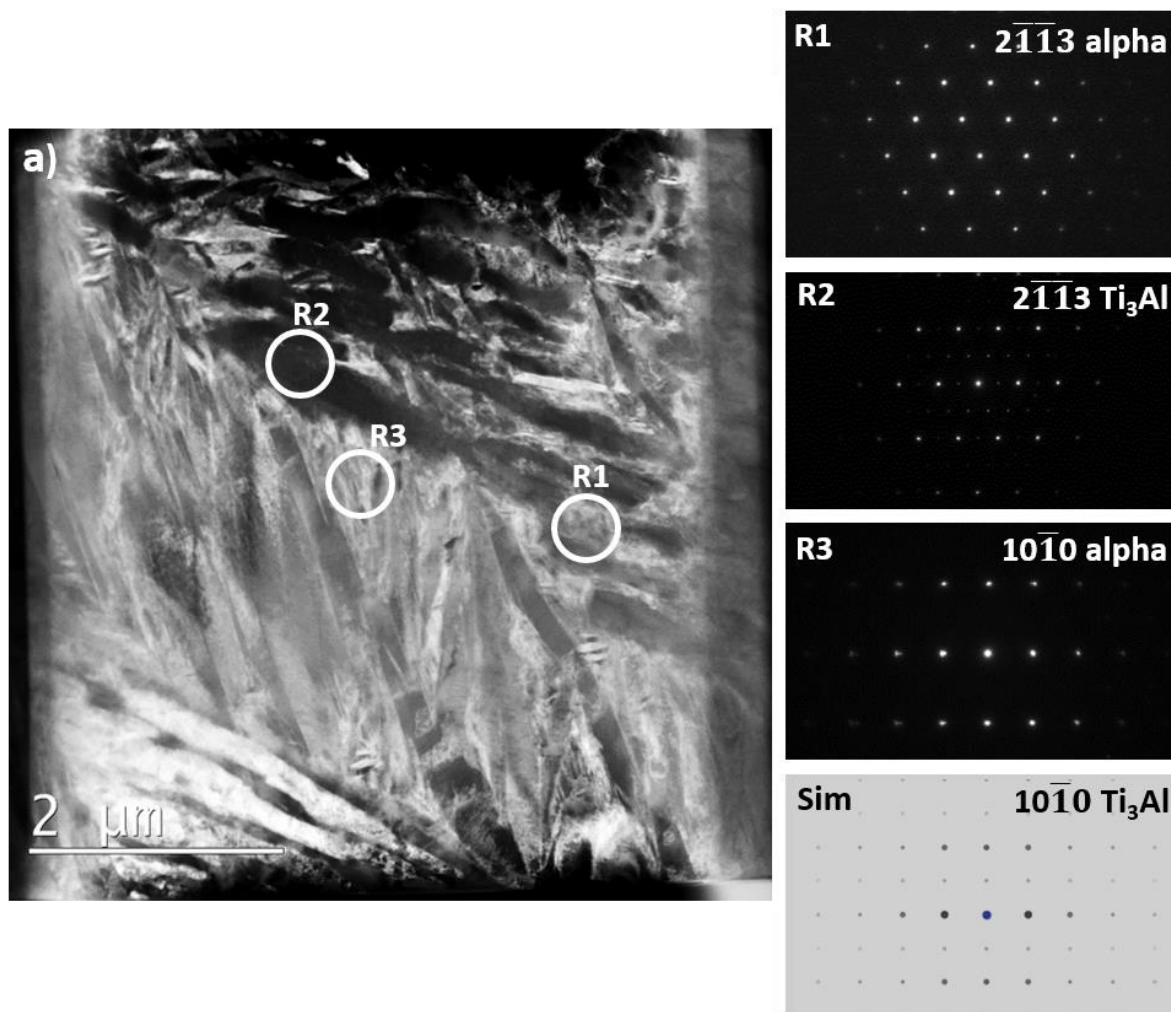


Figure 4. 13: FIB-SEM foil 1 a) HAADF STEM micrograph of 20 at.% hydrogenated Ti-6Al-4V highlighting (in white) the SAD analysed regions R1-R3. Atomic Z-contrast in a) shows that region R2 is Al rich whilst R1 and R3 are Al lean (or V rich). The complementary SAD patterns confirm Ti_3Al phase in the Al rich region R2 and alpha phase in the Al lean (or V rich) regions R1 and R3 at zone axes $[2\bar{1}\bar{1}3]$ Ti_3Al and $[2\bar{1}\bar{1}3]$, $[10\bar{1}0]$ alpha. The simulated (Sim) $[10\bar{1}0]$ Ti_3Al diffraction pattern is included to eliminate HCP crystal ambiguity between $[10\bar{1}0]$ Ti_3Al and $[10\bar{1}0]$ alpha. It confirms that the R3 attained $[10\bar{1}0]$ SAD pattern is alpha and not Ti_3Al .

The SAD analysis in **Figure 4.13** highlights two aspects that are pertinent to the argument. Firstly, it confirms that Ti_3Al phase precipitated in the extensively Al enriched clusters of the hydrogenated sample (R2). Secondly, it confirms the Al lean (or V rich) regions R1 and R3 as HCP phase and not hydrides. The latter aligns with the TKD phase analysis in **Figures 4.9 b)** and **4.10 b)**. Therefore SAD analysis reiterates that hydrogen inadvertently escaped from electron transparent FIB-SEM foils, the escape transformed V rich hydrides to V rich HCP phase without altering the composition. This retained V rich hydride landmarks which could be analyzed post hydride decomposition to establish the effect of hydride precipitates on the microstructure.

4.4.4 Element partitioning at fine hydride precipitates

FIB-SEM foil 3 was extracted from the fine hydrides that precipitate in the lamellae region (see **Figure 4.8 b3**). **Figure 4.14 a, b)** presents EDS maps that show V and Al enrichment at fine hydride landmarks and their neighbouring regions respectively. **Figure 4.14 a)** distinguishes fine hydride landmarks by their characteristic V enrichment. **Figure 4.14 b)** highlights that the fine hydride landmarks have neighbouring Al rich clusters. **Figure 4.14 c)** quantifies the degree of Al enrichment at EDS points 1-5 highlighted in image b). The Al content in the Al rich clusters exceeds 15 at.%Al (EDS points 1, 4), whilst the Al lean hydride landmarks have at most 5 at.%Al (EDS points 2,3,5). This indicates that fine hydrides partitioned Al to neighbouring Al rich clusters where the Al content exceeds 15 at.%Al.

Selected area diffraction was performed at regions R6-R8 and the corresponding SAD patterns are presented as R6-R8 in **Figure 4.14 d)**. The SAD patterns confirm Ti_3Al precipitates in the Al rich clusters R6 and R7 at zone axes $[5\bar{1}\bar{4}6]$, $[10\bar{1}2]$ respectively. They also confirm the V rich hydride landmark R8 as alpha phase at zone axis $[7\bar{2}\bar{5}3]$. The confirmation of V rich hydride landmarks as alpha reiterates that hydrogen inadvertently escaped electron transparent samples. The escape occurred at room temperature and it transformed V rich hydrides to V rich HCP phase. The composition was not altered during the transformation because Al and V have negligible diffusivity⁷⁵ at room temperature (see **Section 2.10.1**). The simulated diffraction patterns validate the attained R6, R7 diffraction patterns to be Ti_3Al and R8 to be alpha at the respective zone axes.

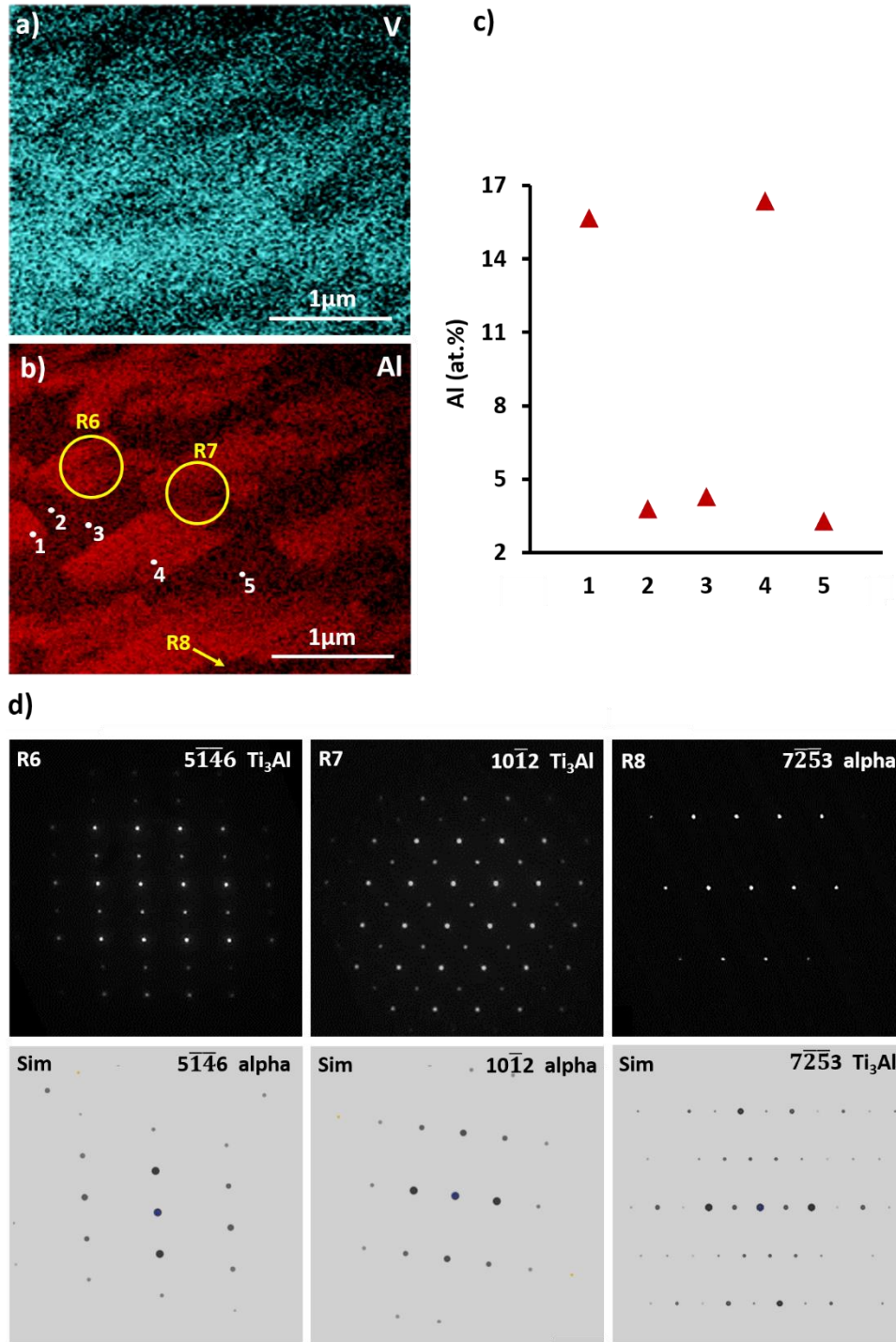


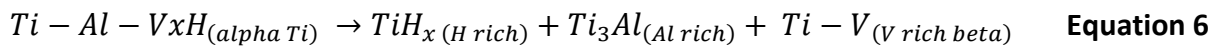
Figure 4. 14: FIB-SEM foil 3 a-b) EDS maps showing a) V rich hydride landmarks and b) their neighbouring Al rich clusters. The Al concentration was analysed at EDS points 1-5 in b) and presented in c). Similarly, SAD was performed at regions R6-R8 in b) and complementary SAD patterns are presented in d). Images a-b) show that fine hydride precipitates partitioned Al to neighbouring Al rich clusters. Image c) quantifies that the Al concentration at Al rich points 1, 4 exceeds 15 at.%Al whilst the Al lean points (2,3,5) have at most 5 at.% Al. The SAD patterns in d) confirm Ti_3Al at Al rich regions (R6, R7) and α at the Al lean region (R8) at zone axes $[5\bar{1}46]$, $[10\bar{1}2]$ and $[7\bar{2}53]$ respectively. The absence or presence of superlattice reflections in the simulated (Sim) patterns confirm that the attained $[5\bar{1}46]$, $[10\bar{1}2]$ patterns are Ti_3Al (not α) and the $[7\bar{2}53]$ pattern is α not Ti_3Al respectively.

4.5 Elements of hydrogenation-disproportionation in hydrogenated Ti-6Al-4V

4.5.1 Theory and expected outcomes

A disproportionation reaction is a chemical reaction where a molecule transforms into two or more dissimilar products that are different chemical species.⁷¹ A formulated idea of a hydrogenation-disproportionation reaction in the Ti-6Al-4V context is described using **Equation 6** where:

- Hydrogenation transforms alpha titanium into two or more products (Ti_3Al and beta) that have different chemical composition (are Al rich or V rich).
- Shen et al.^{43, 48} predicts this to proceed through a rejection of Al and V from hydride precipitates to the adjacent matrix, where they form distinct Al rich and V rich regions which stabilise Ti_3Al and beta phases respectively.^{43, 48}



4.5.2 Experimental observations

The evolution of the Ti-6Al-4V microstructure during hydrogenation is summarised by the schematic diagrams in **Figure 4.15 a-f**:

- a. The starting microstructure (simulated cast Ti-6Al-4V) has retained beta (BCC) interlamellae and alpha (HCP) lamellae regions.
- b. Fine V rich beta grains nucleate in the lamellae region because hydrogen's beta stabilising effect increases the volume fraction of beta phase at hydrogenation temperature (650°C).
- c. Cooling from 650°C transforms V rich beta, to V rich alpha. The V rich alpha is saturated in hydrogen because the beta phase dissolves more hydrogen than alpha phase.⁴³
- d. The V rich, and hydrogen saturated alpha transforms to V rich hydrides which induce defects (hydride induced defects) into the matrix.^{51, 52}
- e. The V rich hydrides partition or reject aluminium to form Al enriched clusters in neighbouring microstructure regions.
- f. The Al enriched clusters stabilise nanosized Ti_3Al precipitates.

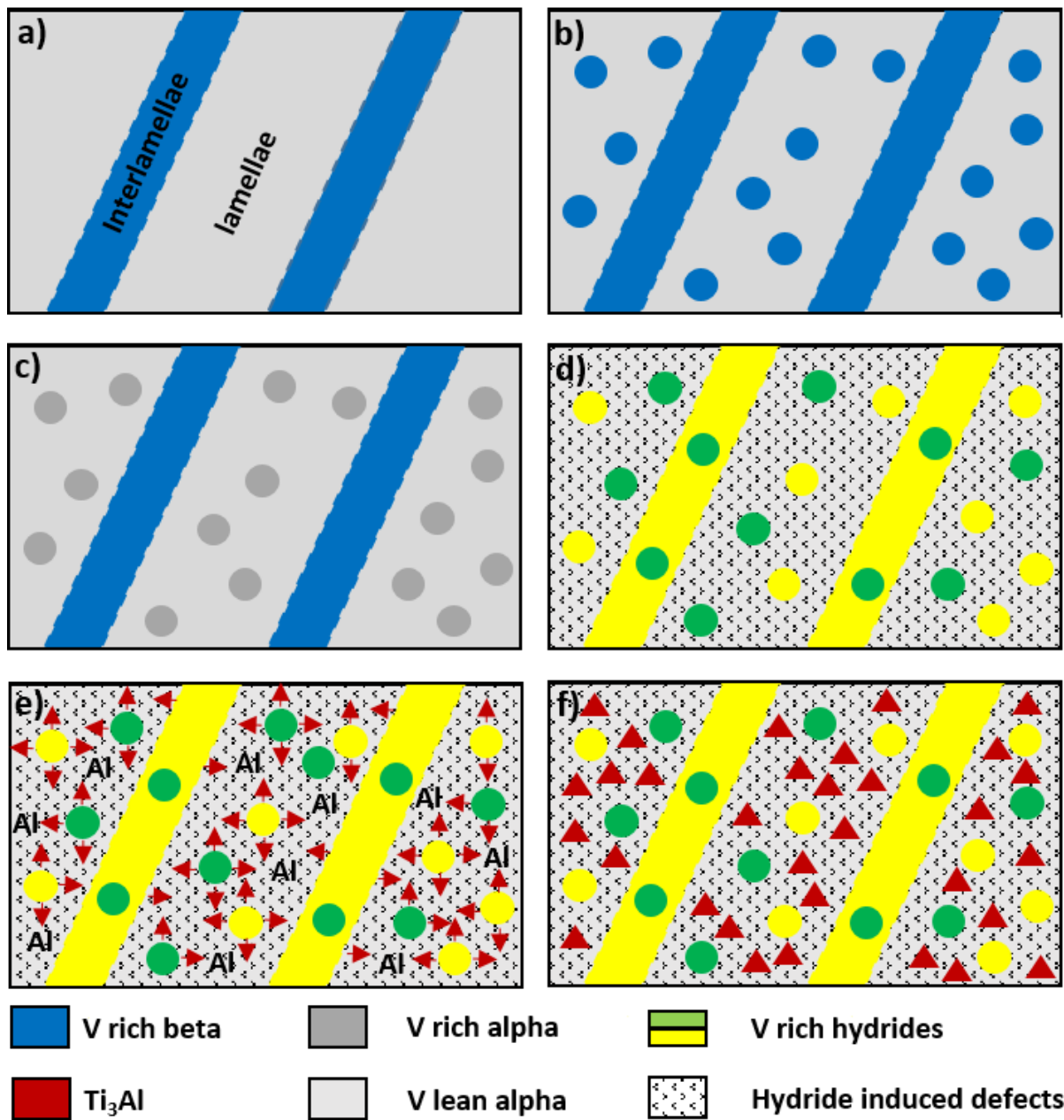
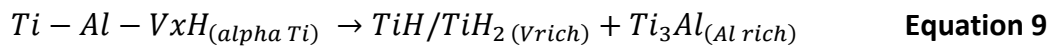


Figure 4. 15: Schematic of the evolution of the hydrogenated Ti-6Al-4V microstructure illustrating the evolution of distinct Al rich and V rich regions which eventually support nucleation of nanosized Ti_3Al precipitates and refined beta grains. Images a-f) illustrate a) simulated cast Ti-6Al-4V b) hydrogen's beta stabilising effect during hydrogenation c) beta to alpha transformation during subsequent cooling d) hydride precipitation and introduction of hydride induced defects in the matrix e) Al partitioning from hydrides to form neighbouring Al rich clusters f) Ti_3Al precipitation in Al rich clusters.

4.5.3 Analysis

Comparing microstructure evolution during hydrogenation to the description of disproportionation; the formulated idea of a disproportionation reaction in the Ti-6Al-4V context, and the proposed features of a Ti-6Al-4V disproportionation reaction, shows that the hydrogenated microstructure has elements of a hydrogenation-disproportionation reaction.

This is because hydrogenation transformed lamellae alpha into distinct Al rich and V rich regions which ultimately stabilised Ti_3Al precipitates and beta grains (**Chapter 5** will uncover that refined beta grains nucleate at V rich regions after hydride decomposition). Therefore the hydrogenation-disproportionation half reaction that accounts for Ti-6Al-4V microstructure evolution (during hydrogenation) can be described by **Equation 9**;



The hydrogenated microstructure demonstrates some microstructure evolution elements that are proposed to occur during hydrogenation-disproportionation. However, it does not show all of the proposed elements;

- *The proposed elements that reflect in hydrogenated Ti-6Al-4V*
Hydride precipitates are lean in aluminium and they have neighbouring Al enriched regions where the degree of Al enrichment stabilises Ti_3Al precipitates.
- *The proposed elements that do not reflect in hydrogenated Ti-6Al-4V*
Hydride precipitates are rich in vanadium and this indicates that vanadium was not rejected from hydride precipitates as proposed in Shen et al.^{43, 48} (see **Section 2.6.2.1**).

Therefore, **Section 4.5** supports the hypothesis which states that hydrogenation-disproportionation can account for the promotion of Ti_3Al formation in hydrogen treated Ti-6Al-4V. The unexpected but observed enrichment of hydrides with vanadium unveils that refined beta grains nucleate from decomposing hydride precipitates, and not V rich regions which form when hydrides reject vanadium.

4.6 Summary of the hydrogenated Ti-6Al-4V microstructure

4.6.1 The influence of hydrogen on phase constitution and composition

Alloyed hydrogen stabilised BCC phase and decreased the sub-transus HCP volume fraction. X-ray diffraction confirmed hydrogen's beta stabilising effect; it showed additional BCC peaks in hydrogenated Ti-6Al-4V which were not observed in non-hydrogenated Ti-6Al-4V.

The beta stabilising effect reduced the subtransus HCP volume fraction and this promoted an enrichment of the reduced HCP volume fraction with Al. Similarly, the BCC volume fraction was enriched in vanadium. Cooling hydrogenated Ti-6Al-4V to room temperature transformed the V rich BCC to V rich alpha and ultimately V rich hydrides (TiH and TiH₂).

Bulk XRD and EBSD analysis confirmed hydride precipitates in 20 at.% hydrogenated Ti-6Al-4V. However, hydride precipitates were not confirmed by high resolution techniques (TKD and SAD) in electron transparent samples. This is because hydrogen inadvertently escaped from electron transparent samples after they were exposed to high vacuum. This could happen during FIB-SEM foil extraction or subsequent TKD or TEM analysis.

The inadvertent hydrogen escape transformed V rich hydrides to V rich HCP phase. This was a room temperature transformation driven by hydrogen escape. Therefore it had limited diffusion kinetics to support Al and V diffusion because the diffusivities of Al and V are substantially lower than that of hydrogen. Consequently, the inadvertent hydride transformation did not alter the elemental composition. This was evident in complementary TKD, EDS and SAD analyses which confirmed the prior hydride regions (or hydride landmarks) as V rich HCP phase.

4.6.2 Effect of inadvertent room temperature hydrogen escape on phase constitution and composition

Notwithstanding the inadvertent hydrogen escape which transformed vanadium rich hydrides to vanadium rich alpha, the effect of hydrides on the microstructure could still be investigated from prior hydride regions or hydride landmarks which were characteristically rich in vanadium.

The vanadium enrichment was not altered during the inadvertent hydride transformation because of the slow diffusion kinetics of V and Al at room temperature. More importantly, the hydride induced partitioning and clustering of aluminium was retained. Therefore, the landmark “prior hydride regions” retained traceable information which enabled a post hydride decomposition analysis of the effect of hydride precipitates on the microstructure. This information uncovered the intimate relationship between hydrogen and Ti_3Al .

4.6.3 The intimate relationship between hydrogen and Ti_3Al

Alloyed hydrogen (20 at.%H) precipitated TiH and TiH_2 hydrides which partitioned Al to form Al rich clusters, where the extent of Al enrichment exceeds the critical Al concentration that stabilises Ti_3Al precipitates. The maximum solubility of Al in alpha is 10 at.%Al,⁸² therefore at least 11 at.%Al⁸³ is required to precipitate Ti_3Al in alpha. In this study, Ti_3Al precipitation was observed at Al concentrations which exceeded 13 at.% Al.

4.6.4 Elements of hydrogenation-disproportionation in hydrogenated Ti-6Al-4V

The hydrogenated Ti-6Al-4V microstructure has elements of a disproportionated microstructure because hydrogenation transformed lamellae alpha into distinct Al rich and V rich regions. This proceeded through a hydride induced partitioning of Al to neighbouring microstructure regions, where the partitioned Al formed Al rich clusters that stabilised Ti_3Al precipitates. However, hydrides did not reject vanadium as proposed in Shen et al.^{43, 48} The hydrogenated microstructure has distinct V rich regions because hydrides retain the vanadium enrichment from the parent beta grain. The effect of hydrogen promoted Ti_3Al precipitates on the tensile performance of hydrogenated and dehydrogenated Ti-6Al-4V is discussed in **Chapter 5**.

CHAPTER 5: MICROSTRUCTURE AND TENSILE PROPERTY RELATIONSHIPS IN HDH TREATED Ti-6Al-4V

Chapter 4 showed that 20 at.% alloyed hydrogen precipitates Ti-H and Ti-H₂ hydrides which partition the microstructure to form Al rich clusters which stabilise Ti₃Al. **Chapter 5** evaluates the effect of hydrogenation-dehydrogenation (HDH) treatment on tensile property performance with particular focus on the effect of Ti₃Al on ductility. It demonstrates the relationship between dehydrogenation temperature, degree of microstructure recombination and tensile performance.

Simulated cast Ti-6Al-4V rods were hydrogenated at 650°C for 12 hours to alloy 20 at.%H. The hydrogenated rods were subsequently dehydrogenated for 3 hours at: 675°C (HDH 675), 700°C (HDH 700), 725°C (HDH 725) and 750°C (HDH 750). A control treatment (control 675) was prepared by vacuum annealing at 650°C for 12 hours and subsequently vacuum annealing for 3 hours at 675°C. Microstructure characterisation was performed using: optical microscopy, X-ray diffraction (XRD), electron backscatter diffraction (EBSD), energy dispersive spectroscopy (EDS), high angle annular dark field STEM (HAADF STEM) and selected area diffraction (SAD). **Chapter 5** initiates by confirming hydrogen escape during dehydrogenation. It proceeds to evaluate the microstructure and tensile property relationships of HDH treated Ti-6Al-4V. It then demonstrates the relationship between the desorption (dehydrogenation) temperature, the degree of recombination and the tensile performance.

Chapter 5 concludes that HDH improves tensile strength by approximately 100 MPa but it also reduces tensile ductility. The loss in ductility at lower dehydrogenation temperatures is not caused by residual hydrogen. Even though there is a possibility that an infinitesimal hydrogen concentration can be retained in the 675°C dehydrogenated sample. This residual hydrogen concentration would not be sufficient to stabilise hydrides nor embrittle the sample. **Chapter 5** shows that Ti₃Al precipitates reduced ductility, and their detrimental effect on ductility can be eliminated by increasing the dehydrogenation temperature to 750°C. The HDH 750 treatment improves the tensile performance of simulated castings to extents that meet the performance standards for wrought Ti-6Al-4V (see the ASTM F1472 standard).

5.1 Mapping hydrogen escape during dehydrogenation or desorption

Hydrogen escape was monitored by observing the vacuum profile during the heating, 3 hour annealing and cooling stages of the 675°C and 750°C dehydrogenation or vacuum annealing treatments.

Figure 5.1 a, b) compares the vacuum profiles of non-hydrogenated (red) and hydrogenated Ti-6Al-4V (blue) samples which were dehydrogenated or vacuum annealed at a) 675°C and b) 750°C. The samples were heated at 5°C/min to controller temperatures of a) 775°C and b) 850°C which correspond to thermocouple temperatures of a) 675°C and b) 750°C. **Figure 5.1 a, b)** also shows the temperature profile of the dehydrogenation or vacuum annealing experiments which encapsulates temperatures that are above 400°C. The temperature profile in **Figure 5.1 a)** incorporates the heating, 3 hour hold and cooling stages. Comparatively, the profile in **Figure 5.1 b)** incorporates the heating and 3 hour hold stages.

Figure 5.1 a) shows that non-hydrogenated samples maintain a constant vacuum increase throughout the 675°C vacuum annealing treatment. It took approximately 4 hours (280 minutes) for the vacuum to increase from 6×10^{-5} mbar to 1×10^{-5} mbar in non-hydrogenated samples.

Conversely, hydrogenated samples decrease the vacuum because of hydrogen escape. The vacuum decrease occurs from 410°C and this temperature marks the onset of the hydrogen escape window. The hydrogen escape window encompasses annealing temperatures that are above 410°C. In this window, the rate of hydrogen escape peaks at 150 minutes (which corresponds to a thermocouple temperature of 630°C) and gradually decreases thereafter.

Significant hydrogen escape occurred during 675°C dehydrogenation:

- This is because at the end of the 3 hour soak at 675°C, the vacuum level of hydrogenated samples (3.8×10^{-4} mbar) is not equivalent to the vacuum experienced by the non-hydrogenated samples. However, it is sufficiently close to conclude that the hydrogen levels are negligible.

- In addition, vacuum levels which are comparable to the non-hydrogenated sample (4.5×10^{-5} mbar) are achieved before the end of the hydrogen escape window.

Admittedly, there is a possibility that the 675°C dehydrogenation experiment could retain an infinitesimal concentration of residual hydrogen in the sample. This residual hydrogen concentration would not be sufficient to stabilise hydride phase nor embrittle the sample. This is supported by XRD and EBSD analyses (discussed in **Section 5.4**) which confirm the absence of hydrides in the 675°C dehydrogenated sample.

Figure 5.1 b) reiterates the observations from **Figure 5.1 a)**. Non-hydrogenated samples maintain a constant vacuum increase during a 750°C vacuum annealing treatment. Similarly, it takes approximately 4 hours (230 minutes) for the vacuum to increase from 5×10^{-5} mbar to 1×10^{-5} mbar in non-hydrogenated samples.

Conversely, hydrogenated samples decrease the vacuum above 410°C because of hydrogen escape. Similarly, the hydrogen escape rate peaks at 150 minutes and it gradually decreases thereafter. Consequently, there is a gradual improvement in vacuum after 150 minutes.

Full hydrogen escape is achieved during the 750°C dehydrogenation:

- This is because the vacuum level of hydrogenated samples is equivalent to the vacuum experienced by the non-hydrogenated samples at the end of the 3 hour soak at 750°C.
- In addition, high vacuum levels which are comparable to non-hydrogenated samples (1.9×10^{-5} mbar) are achieved within the hydrogen escape window.

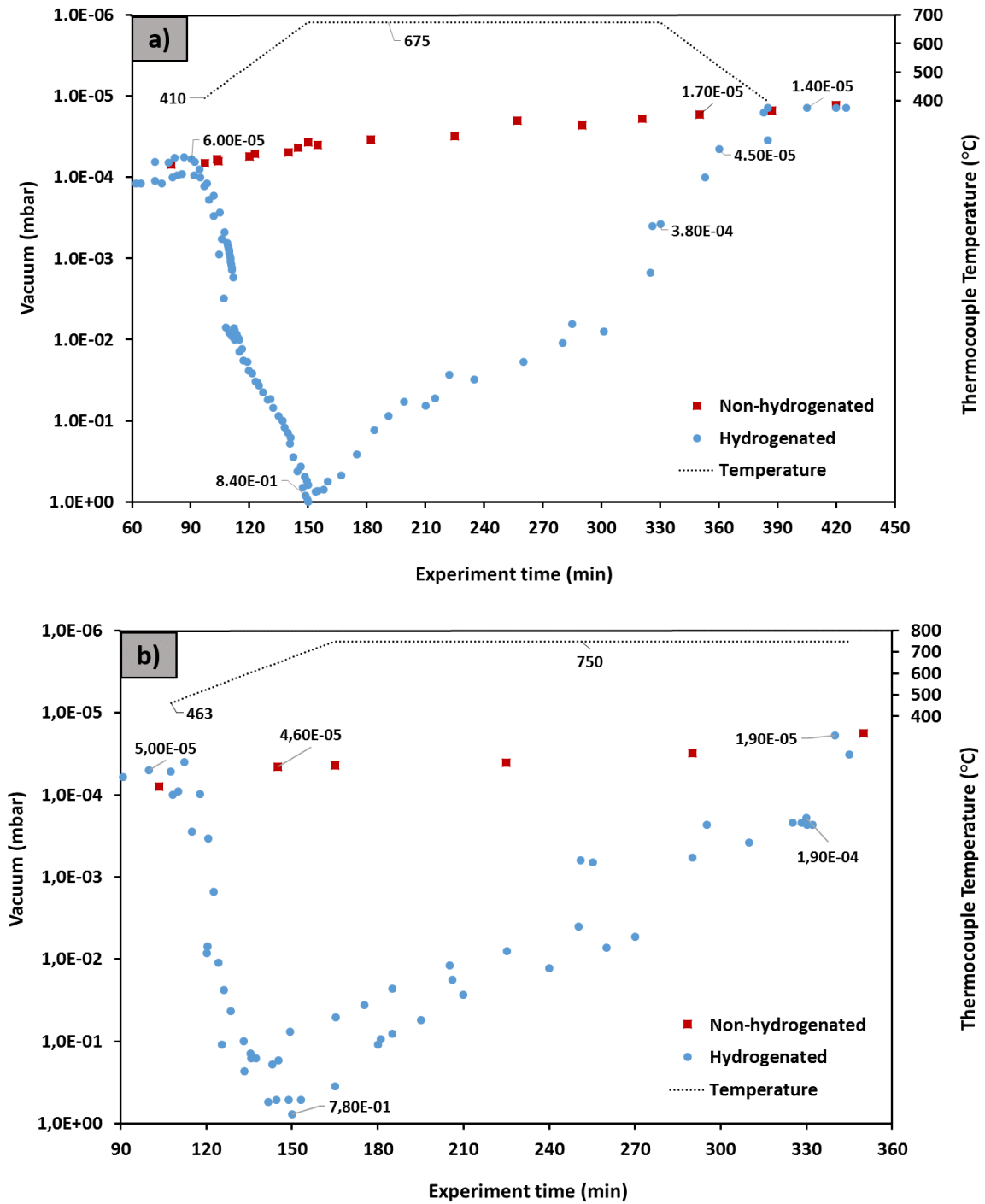


Figure 5. 1: Vacuum profiles of non-hydrogenated (red) and hydrogenated (blue) Ti-6Al-4V attained during a 3 hour vacuum anneal or dehydrogenation at a) 675°C or b) 750°C. Non-hydrogenated samples maintain a constant vacuum increase during the experiment. Hydrogenated samples decrease the vacuum above 410°C and this marks the onset of the hydrogen escape window. The rate of hydrogen escape peaks at 150 minutes experiment time and gradually decreases thereafter. Significant hydrogen escape is achieved during 675°C dehydrogenation, but there is a possibility that an infinitesimal hydrogen concentration is retained in the sample. Full hydrogen escape is achieved during 750°C dehydrogenation. Both instances show that vacuum levels which are comparable to the non-hydrogenated samples are achieved within the hydrogen escape window.

5.2 Optical micrographs of HDH treated microstructures

Figure 5.2 compares the optical micrographs of simulated cast Ti-6Al-4V to HDH treated Ti-6Al-4V which was dehydrogenated at 675°C (HDH 675) and 750°C (HDH 750). In **Figure 5.2**, all microstructures have coarse laths. However, hydrogen treated microstructures (HDH 675 and HDH 750) have refined grains within the coarse laths. This refinement is caused by hydrogen treatment because it is not observed in the control 675 sample.

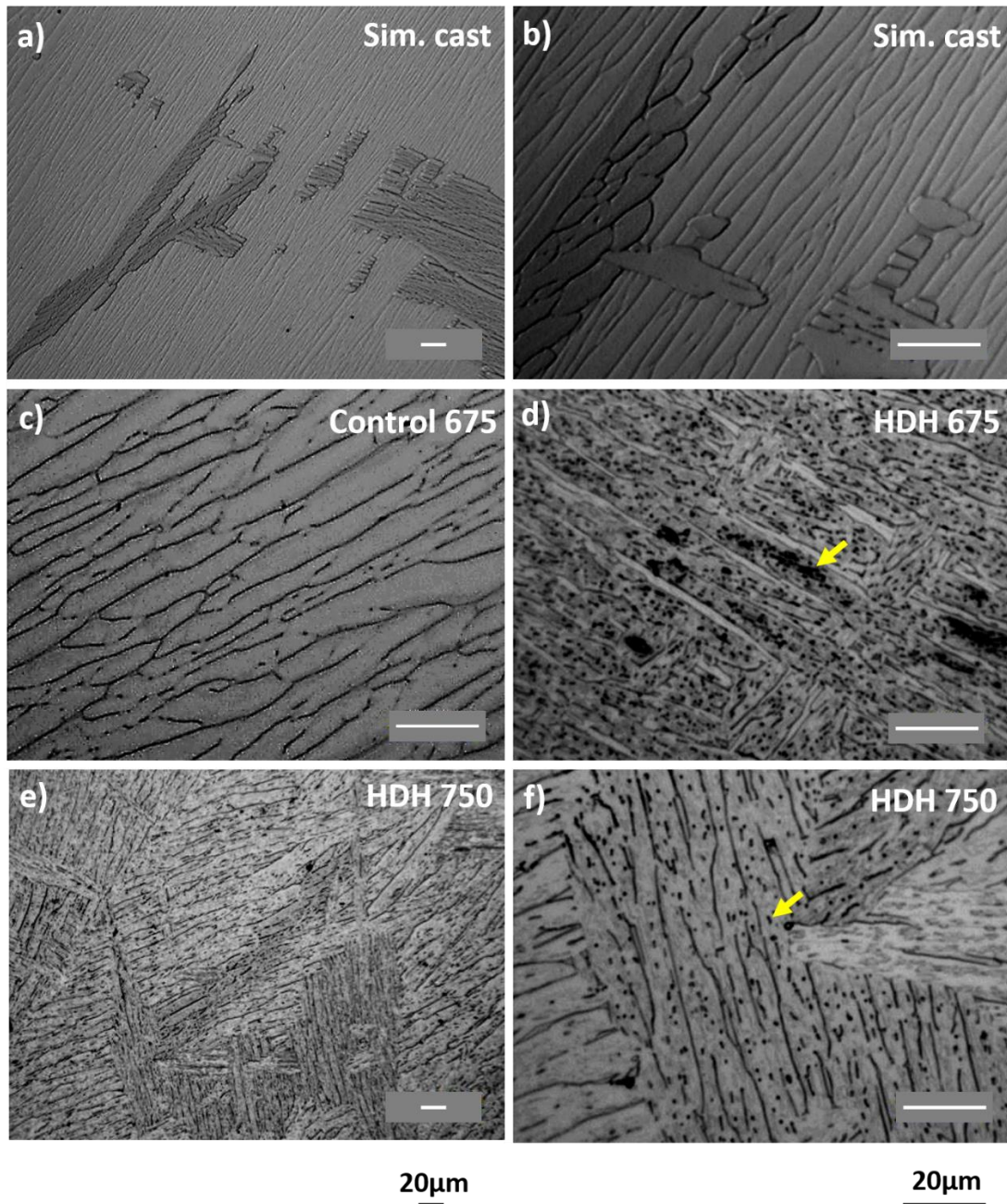


Figure 5. 2: Optical micrographs of a- b) simulated cast (Sim. cast), c) control 675 d) HDH 675 and e-f) HDH 750 treated Ti-6Al-4V. Hydrogen treated samples have refined grains (highlighted in yellow) within their coarse laths. The refined grains are not observed in non-hydrogen treated samples (simulated cast and control 675).

5.3 Tensile performance of HDH treated microstructures

Figure 5.3 compares the tensile performance of hydrogenated-dehydrogenated (HDH) Ti-6Al-4V to simulated cast Ti-6Al-4V and the control experiment (control 675). For ease of reference, the tensile performance data was extracted from **Figure 5.3** and tabulated in **Table 5.1**. In **Table 5.1**, the tensile performance is compared to the performance requirements from the American Society for Testing and Materials (ASTM) for wrought (ASTM F1472) and cast (ASTM F1108-14) Ti-6Al-4V. In **Table 5.1**, average values are quoted to cater for scatter which is up to 20 MPa (for strength) and 1.5% elongation for ductility.

Figure 5.3 and **Table 5.1** show that simulated cast Ti-6Al-4V has a yield strength (YS) of 760 MPa, an ultimate tensile strength (UTS) 930 MPa and 10% ductility. The tensile performance of simulated cast Ti-6Al-4V meets the performance requirements for Ti-6Al-4V castings stipulated in the ASTM F1108–14 standard.

Annealing and subsequently vacuum annealing simulated cast Ti-6Al-4V at 675°C (control 675°C) causes up to 30 MPa loss in strength. The yield strength decreases by 30 MPa (760 MPa to 730 MPa) and the ultimate tensile strength decreases by 24 MPa (930 MPa to 906 MPa) respectively. Full ductility of 10% is retained after vacuum annealing non-hydrogen treated Ti-6Al-4V at 675°C. In comparison, hydrogenating and subsequently dehydrogenating simulated cast Ti-6Al-4V at 675°C (HDH 675) increases the yield strength (YS) by approximately 84 MPa (760 MPa to 844 MPa) and the ultimate tensile strength by 57 MPa (930 MPa to 987 MPa). The strength increase in HDH 675 samples is accompanied by a 75% ductility loss from 10% to 2.5% elongation. The strength increase and the ductility loss observed in the HDH 675 sample is caused by hydrogen treatment.

Increasing the dehydrogenation temperature to 700°C and 725°C does not significantly change the yield strength and the ultimate tensile strength. It maintains the approximate 70-80 MPa yield and the 57-70 MPa ultimate tensile strength improvement when compared to the simulated cast Ti-6Al-4V sample. Similarly, ductility is not significantly recovered after dehydrogenating at 700°C. However, up to 47% ductility is recovered after dehydrogenating at 725°C.

The ductility does not significantly improve after dehydrogenating at 700°C. The HDH 700 sample recovered less than 10% ductility from 2.5% to 3.3% elongation which falls within the expected 1.5% elongation scatter. Therefore the HDH 700 ductility is not significantly different from the HDH 675 sample.

Comparatively, the ductility improves after dehydrogenating at 725°C. The HDH 725 sample recovered 47% ductility from 2.5% to 7.2% elongation. Therefore, the HDH 725 treated sample has the improved strength properties and up to 72% of the benchmark ductility.

Dehydrogenating at 750°C restored full ductility and improved the yield (by 70 MPa) and the ultimate tensile strength (by 100 MPa). The HDH 750 sample recovered 75% ductility from 2.5% to 10% elongation. The recovered ductility enhanced the degree of work hardening and ultimately improved the ultimate tensile strength by 100 MPa (930 MPa to 1030 MPa).

The wrought Ti-6Al-4V microstructure is preferred for in-service applications because it provides the best combination of strength and ductility. The ASTM F1472 standard stipulates the required strength and ductility for wrought Ti-6Al-4V as 825-860 (YS), 895-930 (UTS) and a minimum 10% elongation.⁹⁵ Simulated cast and the control 675 meet the ductility requirements but not the strength requirements. In comparison, HDH treated Ti-6Al-4V that is dehydrogenated below 750°C meets the strength but not the ductility requirements. However, HDH treated Ti-6Al-4V that is dehydrogenated at 750°C meets the strength and ductility requirements for in-service applications.

Table 5. 1: The effect of increasing the vacuum annealing or dehydrogenation temperature from 675°C to 750°C on tensile performance of tempered martensite.

Heat treatment	YS (MPa)	UTS (MPa)	Elongation (%)
ASTM F1108 – 14 ⁹⁶	758	860	≥8
Simulated cast Ti-6Al-4V	760	930	10
Control 675	730	906	10
HDH 675	844	987	2.5
HDH 700	848	1000	3.3
HDH 725	835	993	7.2
HDH 750	830	1030	10
ASTM F1472 ⁹⁵	825-860	895-930	≥10

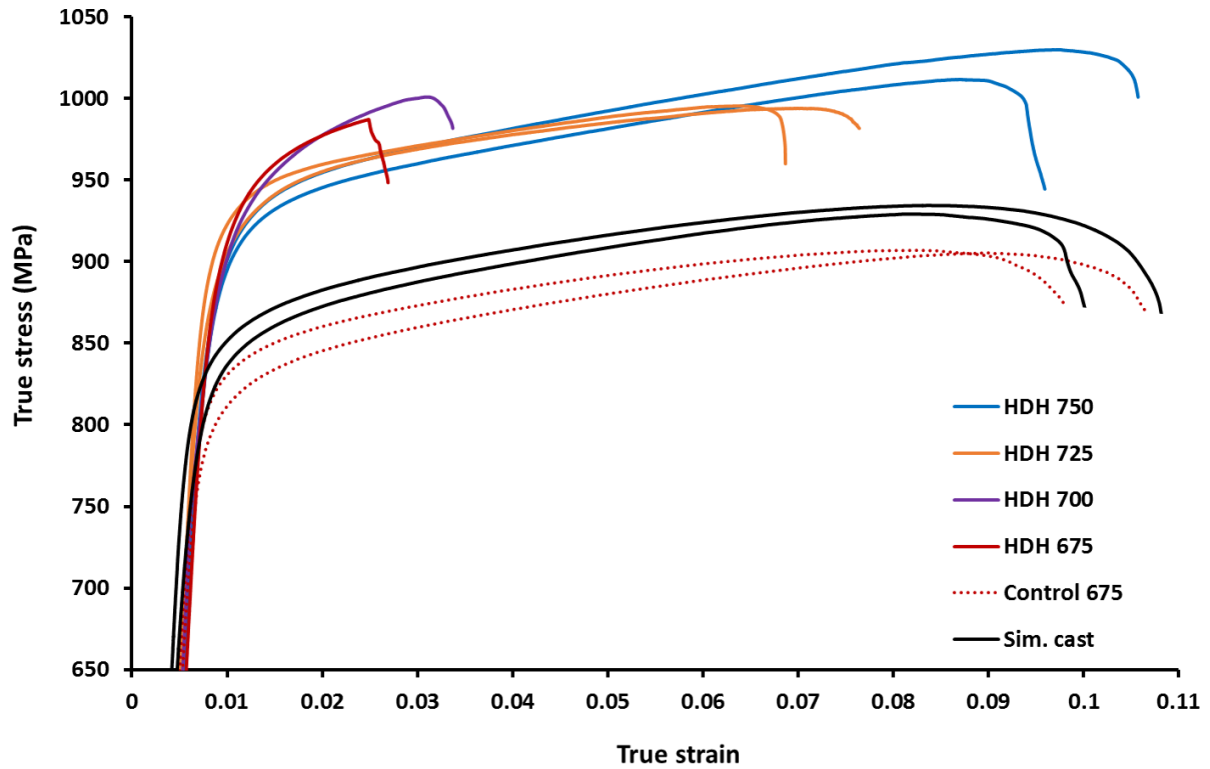


Figure 5. 3 Tensile performance of simulated cast (black) and HDH treated microstructures: HDH 750 (blue), HDH 725 (orange), HDH 700 (purple), HDH 675 (solid red). The dotted red lines represent the control 675 treatment performed in the absence of hydrogen.

Ductility loss in hydrogen treated Ti-6Al-4V is typically attributed to embrittlement from residual hydrogen or hydrides. However, in this instance it cannot be attributed to either residual hydrogen or hydrides. Even though there is a possibility that the 675°C dehydrogenation experiment can retain an infinitesimal concentration of residual hydrogen in the sample, this residual hydrogen concentration would not be sufficient to stabilise hydride phase nor embrittle the sample.

In addition, the ductility loss cannot be attributed to oxygen contamination. This is because the control 675 treatment undergoes the same heat treatment cycle as HDH 675 but it still maintains full ductility. In the case of oxygen contamination, the ductility loss would intensify with increasing temperature. This is contrary to what is observed in HDH treated samples, where ductility improves with increasing temperature. Therefore, the ductility loss in HDH treated samples is closely linked to the response of hydrogen treated microstructures to dehydrogenation or desorption temperature.

5.4 The effect of dehydrogenation temperature on microstructure recombination

Section 5.4 uses XRD, EBSD and TEM to elaborate on the ductility loss in HDH treated samples. It establishes a relationship between dehydrogenation temperature and the extent of microstructure recombination. Dehydrogenation or desorption recombines hydride partitioned microstructures. The degree of microstructure recombination is measured by the extent to which the hydride induced partitioning products are eliminated from the microstructure.

Chapter 4 showed that 20 at.% alloyed hydrogen precipitates Ti-H or Ti-H₂ hydrides. The hydrides partition Al from its Ti-Al couple to form Al rich clusters that stabilise Ti₃Al precipitates. Therefore full microstructure recombination not only depends on hydride decomposition, but it also depends on Ti₃Al dissolution. Hydrogen escape decomposes hydride precipitates to nucleate refined equilibrium alpha and beta phases. However, hydrogen escape does not equally dissolve Ti₃Al precipitates. The precipitated Ti₃Al dissolves at elevated annealing temperatures of at least 750°C.⁴²

5.4.1 XRD analysis of phase evolution during HDH treatment

Figure 5.4 a-b) compares the phase constitution in simulated cast, hydrogenated, HDH treated Ti-6Al-4V. **Figure 5.4 a)** shows that simulated cast Ti-6Al-4V has three main alpha reflections $\alpha_{10\bar{1}0}$, α_{0002} , $\alpha_{10\bar{1}1}$ at 2 theta 35.5°, 38.5°, 40.5° respectively and a β_{110} reflection at 2 theta 39.5° in the 2 theta range of 35°-42°. Alloyed hydrogen caused a lattice expansion which shifted the β_{110} peak from 39.5° to merge with the α_{0002} peak at 38.5°. Alloyed hydrogen also promoted hydride precipitation which is evident in the delta hydride peaks (δ_{111} , δ_{200}).

Hydride phase partitions Al to form Al rich clusters which stabilise Ti₃Al precipitates in the HCP lattice. Alpha and Ti₃Al have the same HCP crystal structure and c-lattice parameter and they cannot be distinguished by EBSD or TKD analysis. However, they have different *a*-lattice parameters of 0.5793nm (Ti₃Al) and 0.293nm (alpha).⁷⁶ X-ray diffraction demonstrates the difference in *a*-lattice parameter as sub-peaks on main HCP reflections. The Ti₃Al sub-peaks cannot be easily distinguished in hydrogenated Ti-6Al-4V because the lattice expansion and

associated high FWHM ratios overshadow Ti_3Al sub-peaks. However, they can be easily identified after hydrogen escape in dehydrogenated Ti-6Al-4V.

Figure 5.4 b) shows that hydrogen escaped and eliminated the lattice expansion which reduced the FWHM ratio in the dehydrogenated Ti-6Al-4V XRD spectra. This restored the position of the β_{110} reflection to 2 theta 39.5° . In addition, hydrogen escape decomposed hydride precipitates to precipitate alpha phase. **Figure 5.4 b)** also shows that Ti_3Al phase is present at all investigated dehydrogenation temperatures which are below 750°C . The Ti_3Al sub-peaks (highlighted by a green arrow) are observed on the $\alpha_{10\bar{1}0}$ and $\alpha_{10\bar{1}1}$ reflections of the HDH 675, HDH 700 and HDH 725 patterns.

The volume fraction of retained Ti_3Al decreases with increasing dehydrogenation temperature from 675°C to 725°C . This is shown in **Figure 5.4 b)** where the intensity of the Ti_3Al sub-peaks decreases with increasing dehydrogenation temperature. The Ti_3Al sub-peaks at the 725°C dehydrogenation temperature have a significantly reduced intensity when compared to their 675°C and 700°C counterparts. This explains why the HDH 725 sample has significantly improved ductility of up to 7.2% elongation compared to the HDH 675 and HDH 700 samples which only have 3.3% elongation (see **Figure 5.7**).

Figure 5.4 b) shows no Ti_3Al sub-peaks on the $\alpha_{10\bar{1}0}$ and $\alpha_{10\bar{1}1}$ peaks of the HDH 750 spectra. This means that the 750°C dehydrogenation temperature either retains an insignificant Ti_3Al volume fraction or fully dissolves Ti_3Al precipitates. This explains why the HDH 750 sample has full ductility of 10% elongation.

The XRD analysis shows that dehydrogenating below 750°C results in partially recombined microstructures. Dehydrogenating below 750°C decomposes hydrides, but full microstructure recombination is not achieved because of Ti_3Al precipitates which are retained in the microstructure. X-ray diffraction does not reflect Ti_3Al sub-peaks at 750°C which means that an insignificant volume fraction of Ti_3Al is present or that the microstructure is fully recombined. The grain refinement and the extent of microstructure recombination in HDH 675 and HDH 750 microstructures was further evaluated by EBSD analysis in **Section 5.4.2**.

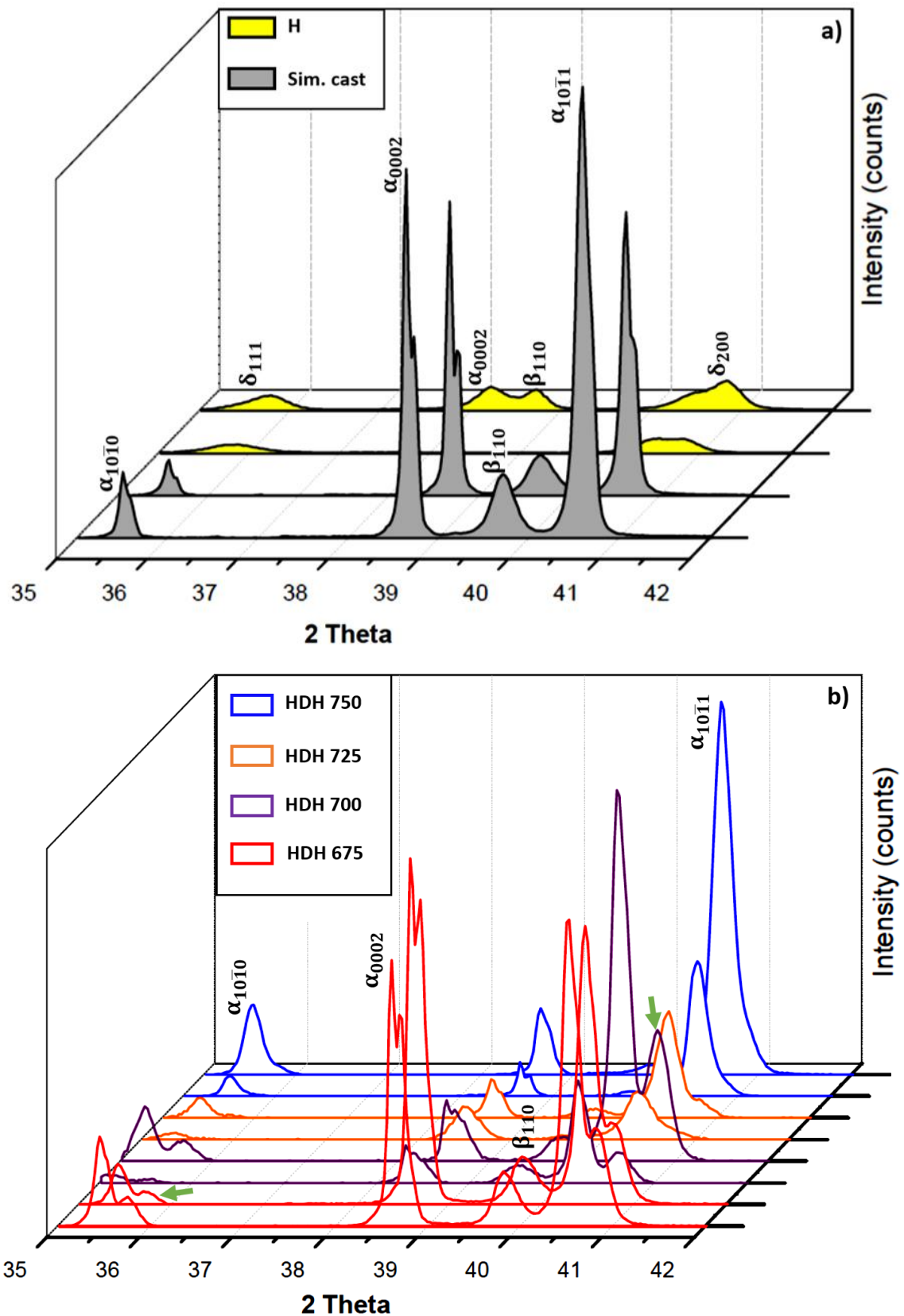


Figure 5. 4: XRD spectra comparing a) simulated cast (Sim. cast), hydrogenated (H) and b) HDH treated Ti-6Al-4V at 2 theta 35°-42°. The Ti₃Al sub-peaks are highlighted in green arrows at $\alpha_{10\bar{1}0}$ and $\alpha_{10\bar{1}1}$ reflections in HDH 675, HDH 700 and HDH 725 samples. There are no observed Ti₃Al sub-peaks at the 750°C dehydrogenation temperature (HDH 750).

5.4.2 Microstructure analysis of HDH 675°C and HDH 750°C treated Ti-6Al-4V

5.4.2.1 Grain refinement in HDH treated Ti-6Al-4V

Figure 5.5 a) and **5.6 a)** are EBSD maps of HDH 675 and HDH 750 microstructures highlighting higher angle grain boundaries (HAGB) with a minimum misorientation angle of 15°. The HAGB show that HDH 675 and HDH 750 microstructures predominantly have coarse HCP laths and interlath regions (for example lath 1). However, they also have fine BCC grains which nucleated at V rich regions within the coarse HCP laths of **Figures 5.5** and **5.6**. This means that fine BCC grains nucleated in the lamellae region after the decomposition of fine V rich hydrides. The nucleation of refined grains within a coarse parent grain was also observed in **Figure 5.2**, and it is typical of hydrogen treated microstructures as observed in **Section 2.6.2.1**.

5.4.2.2 Degree of recombination in HDH treated Ti-6Al-4V

The HDH 675 microstructure is partially recombined because dehydrogenating at 675°C decomposed hydride phase but it retained Ti₃Al precipitates. This is shown in **Figure 5.5 a)** where EBSD phase mapping only confirmed equilibrium alpha and beta phases and no hydride phase in the HDH 675 sample. However, the complementary EDS maps in **Figure 5.5 b, c)** still show an uneven distribution of Al in the HCP phase of the HDH 675 sample. For instance, lath 1 has an HCP crystal structure, it is atypically lean in aluminium (Al) and rich in vanadium (V), and it is neighboured by HCP grains that have Al rich clusters. Before dehydrogenation, lath 1 was a V rich hydride lath that partitioned Al, to form neighbouring Al rich clusters. Dehydrogenating at 675°C did not support sufficient Al diffusion to dissolve the Al rich clusters.

In comparison, the HDH 750 microstructure is significantly recombined: the hydride phase decomposed and Ti₃Al significantly dissolved after dehydrogenating at 750°C. This is shown by EBSD phase mapping in **Figure 5.6 a)** which only confirms alpha, beta phases and no hydride phase in the HDH 750 sample. The EDS maps in **Figure 5.6 b, c)** show the typical partitioning of Al and V towards HCP and BCC phases. They also show a significantly reduced volume fraction of Al rich clusters which are highlighted by the varied Al composition within HCP lath 2. This indicates that the 3 hour dehydrogenation at 750°C does not fully homogenise the Al composition in hydride partitioned microstructures. However, it supports extensive Al diffusion which significantly dissolves Al rich clusters to extents that restore full ductility.

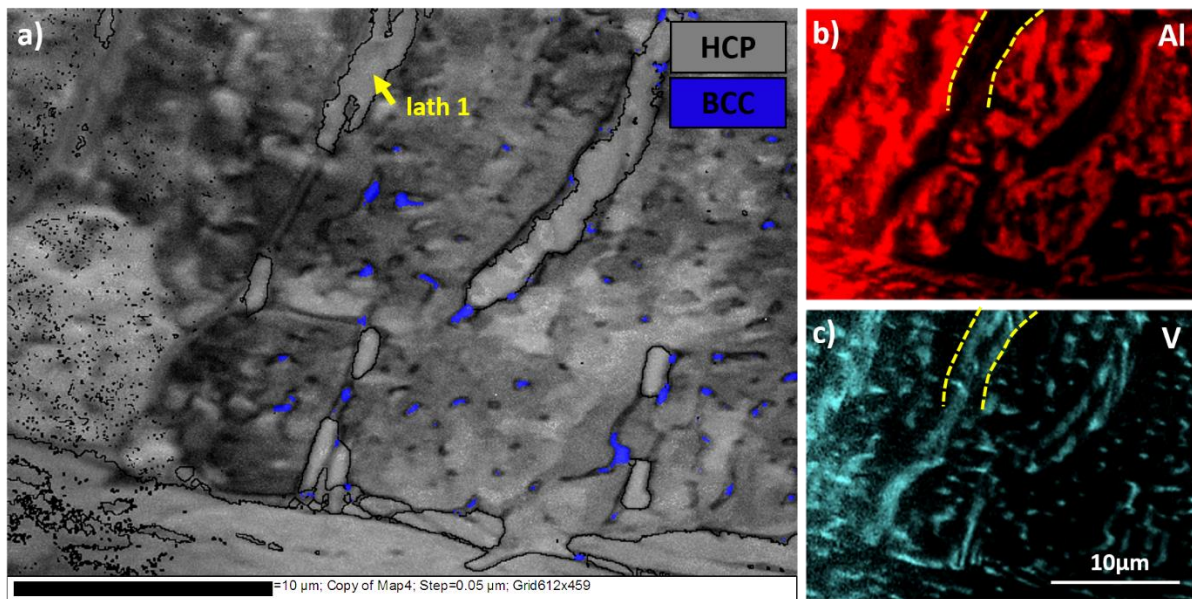


Figure 5. 5: Complementary a) EBSD phase and EDS b) Al, c) V maps showing hydrogenated and 675°C dehydrogenated Ti-6Al-4V. The phase map in a) shows that the HDH 675 sample only has equilibrium beta-BCC (blue) and alpha-HCP (grey) phases and no indexed hydride phase. The corresponding EDS maps in b, c) show a significant variation in Al content in the HCP phase. This is demonstrated in HCP lath 1 (highlighted in yellow) which is atypically lean in Al but has neighbouring HCP grains which have Al rich clusters. Black lines in a) highlight higher angle grain boundaries (HAGB) with a minimum misorientation angle of 15°.

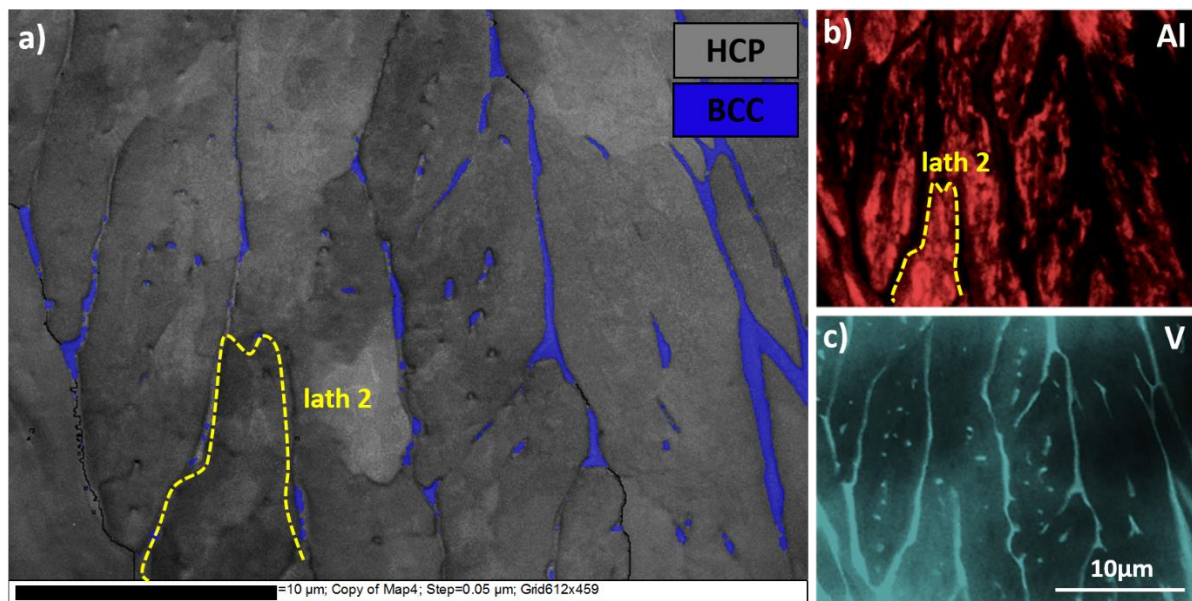


Figure 5. 6: Complementary a) EBSD phase and EDS b) Al, c) V maps showing hydrogenated and 750°C dehydrogenated Ti-6Al-4V. The phase map in a) shows that the HDH 750 sample only has equilibrium beta-BCC (blue) and alpha-HCP (grey) phases and no indexed hydride phase. The EDS maps in b, c) show a typical partitioning of Al and V towards HCP and BCC phases. Image b) also shows a significantly reduced volume fraction of Al rich clusters which are highlighted by the varied Al composition within HCP lath 2. Black lines in a) are HAGB with a minimum misorientation angle of 15°.

5.4.2.3 The degree of Al enrichment in HDH treated Ti-6Al-4V

Figure 5.7 compares the degree of Al enrichment in non-hydrogenated, hydrogenated and HDH treated Ti-6Al-4V (HDH 675 and HDH 750). Non-hydrogenated Ti-6Al-4V includes simulated cast (Sim. cast) and annealed simulated cast (A. Sim. cast).

In **Figure 5.7**, non-hydrogenated Ti-6Al-4V has up to 13 at.%Al content. Alloyed hydrogen precipitates hydrides which partition Al to form Al enriched clusters. Consequently, hydrogenated Ti-6Al-4V has up to 26 at.%Al. Dehydrogenating at 675°C, does not support sufficient Al diffusion to dissolve the Al rich clusters and Ti_3Al precipitates (**Figures 5.4** and **5.5**). Therefore the degree of Al enrichment in the HDH 675 sample remains high at 25 at.%Al. In comparison, dehydrogenating at 750°C supports extensive Al diffusion which significantly dissolves the Al rich clusters and Ti_3Al precipitates (**Figures 5.4** and **5.6**). Therefore the degree of Al enrichment in the HDH 750 sample is reduced to 11 at.%Al which is comparable to the equilibrium Al concentration in non-hydrogenated Ti-6Al-4V.

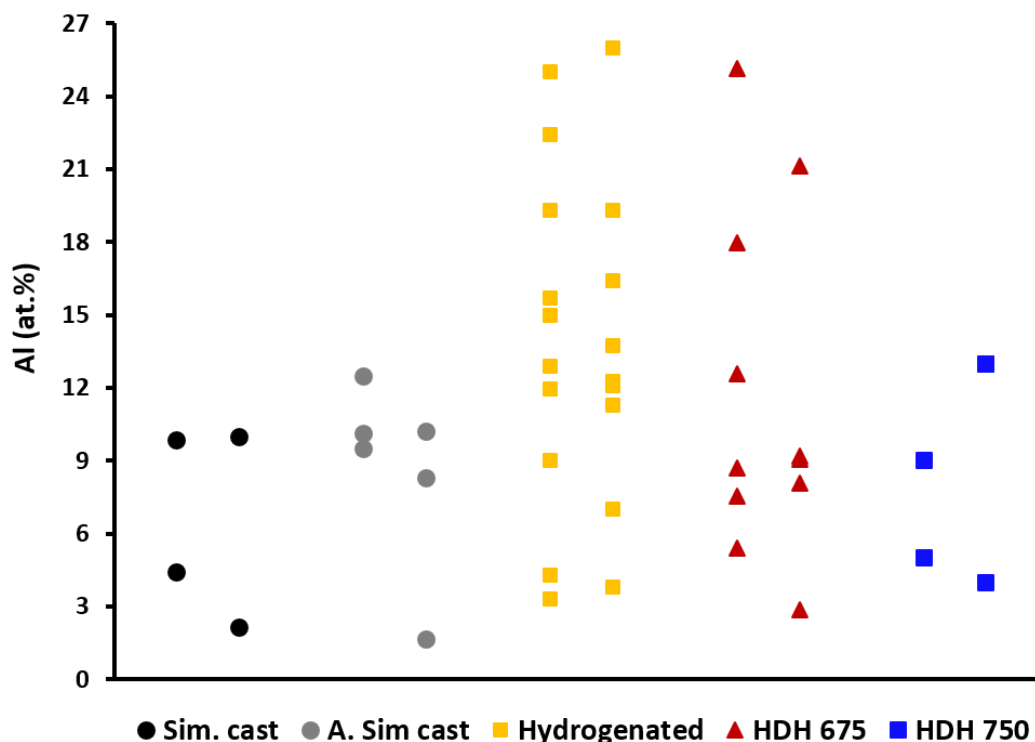


Figure 5. 7: The degree of Al enrichment in non-hydrogenated (Sim. cast and A. Sim. cast), hydrogenated and HDH treated Ti-6Al-4V which was dehydrogenated at 675°C (HDH 675) and 750°C (HDH 750). The degree of Al enrichment in non-hydrogenated Ti-6Al-4V is up to 13 at.%Al. This increases to 26 at.%Al in hydrogenated Ti-6Al-4V due to hydride induced partitioning. It remains at 25 at.%Al after dehydrogenating at 675°C and it significantly decreases to 11 at.%Al after dehydrogenating at 750°C.

5.5 Effect of retained Al rich clusters on tensile ductility

Figure 5.8 a-c) shows complementary a) HAADF STEM and EDS b) V, c) Al maps with their corresponding selected area diffraction patterns attained at the R1 (yellow) and R2 (white) regions of a hydrogenated and 675°C dehydrogenated (HDH 675) Ti-6Al-4V sample.

Figure 5.8 a-c) highlights lath 3 which is rich in vanadium and depleted in aluminium. Lath 3 has a neighbouring Al rich cluster R1 (highlighted in yellow). Before dehydrogenation, lath 3 was a V rich hydride lath that partitioned Al to the neighbouring Al rich cluster R1. Subsequent dehydrogenation at 675°C did not provide sufficient Al diffusion to dissolve the Al rich cluster R1. Consequently, the Al rich cluster R1 retained its extensive Al enrichment. The degree of Al enrichment in the Al rich cluster R1 stabilised Ti_3Al precipitates, and this is confirmed by the R1-SAD pattern at a $[10\bar{1}2]$ zone axis.

The Al rich clusters are the preferred pathway for crack propagation. The green arrow in **Figure 5.8** highlights a crack caused by argon ion damage which occurred when precision ion milling TEM samples to electron transparent thickness. The crack originates from the hole of the electron transparent sample and initially propagates through an Al lean region. The Al lean region R2 was confirmed by R2-SAD to be alpha phase at a $[10\bar{1}1]$ zone axis.

The trajectory of the crack changes direction by approximately 90 degrees when it meets Al rich clusters which SAD confirmed as Ti_3Al phase in R1. This change in direction means that Ti_3Al clusters are the preferred pathway for crack propagation because they provide the least resistance to deformation. Titanium aluminide (Ti_3Al) orders to a D0_{19} structure which reduces the deformation modes of the HCP crystal.⁹⁷ The ordered HCP crystal structure has limited slip systems⁹⁸ (see **Section 2.10.3**) and this explains the 75% ductility loss in the HDH 675 sample.

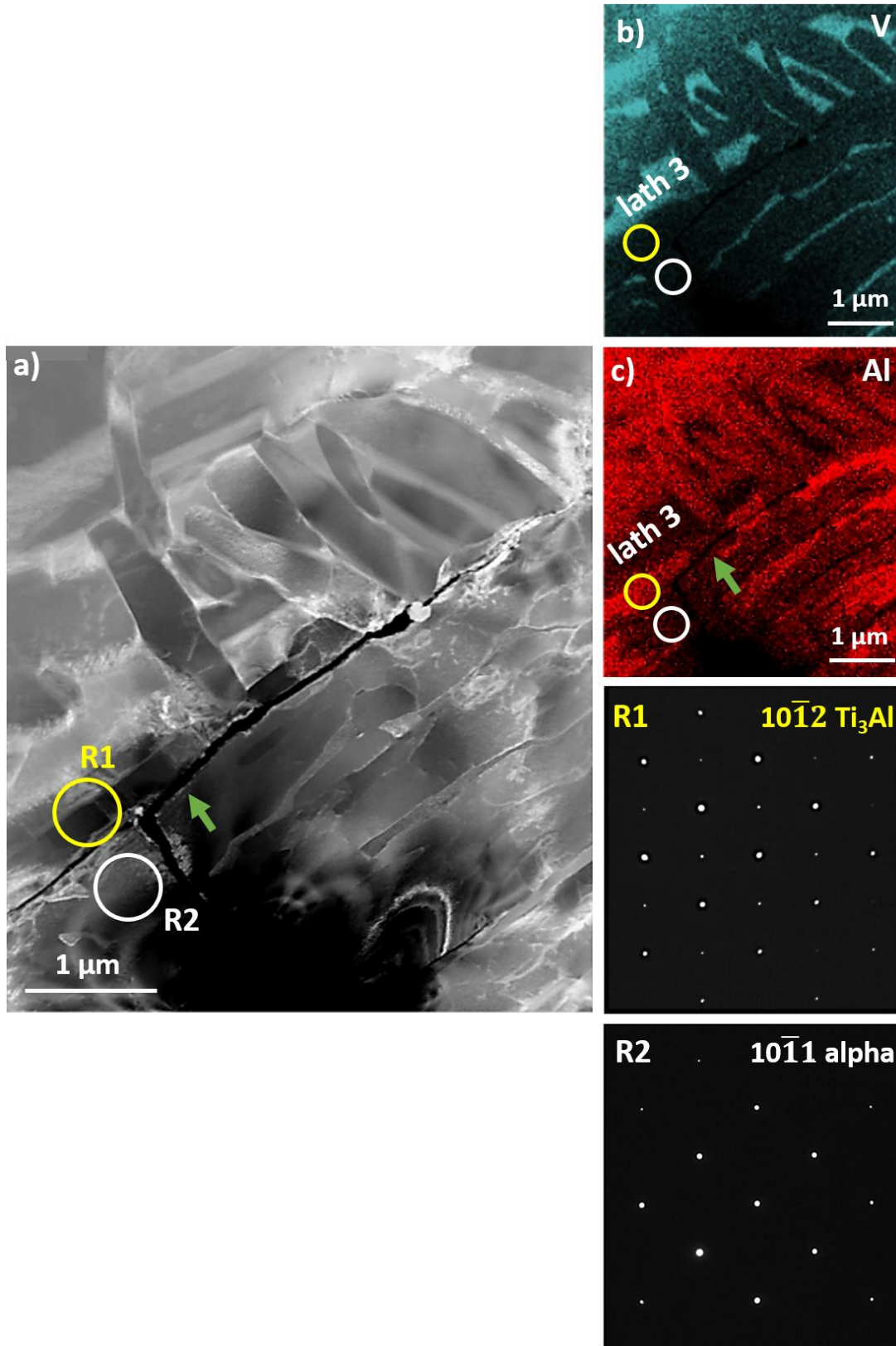


Figure 5. 8: a) HAADF STEM and complementary EDS b) V c) Al maps of HDH 675 treated Ti-6Al-4V. b) The green arrow in a) highlights a crack propagating through the Al rich clusters. The R1 and R2 SAD patterns were attained at the Al rich cluster R1 (yellow) and its Al lean neighbouring region R2 (white), they confirm Ti_3Al , alpha at $[10\bar{1}2]$, $[10\bar{1}1]$ zone axes respectively.

5.6 Summary of hydrogenation-dehydrogenation (HDH)

Simulated cast Ti-6Al-4V tensile rods were hydrogenated at 650°C for 12 hours to alloy 20 at.%H. The hydrogenated rods were subsequently dehydrogenated for 3 hours at varied temperatures namely; 675°C (HDH 675), 700°C (HDH 700), 725°C (HDH 725) and 750°C (HDH 750). A control treatment (control 675) was prepared by vacuum annealing at 650°C for 12 hours and subsequently vacuum annealing for 3 hours at 675°C. The treated rods were subsequently machined to the ASTM- E8/E8M – 13a tensile sample specifications.⁸⁷

5.6.1 HDH treatment and grain refinement

Hydrogenation precipitates V rich lath hydrides (in the interlamellae region) and fine hydrides (in the lamellae region) of simulated cast Ti-6Al-4V. Subsequent dehydrogenation, decomposes the hydride precipitates and nucleates refined BCC grains at the V rich regions. Substantial grain refinement occurs in the lamellae region because fine BCC grains nucleate within a coarse parent HCP grain and this results in strength improvements.

5.6.2 HDH treatment and tensile strength

Hydrogenation-dehydrogenation (HDH) treatment improves the tensile strength of simulated castings by 80 MPa (yield strength) and 100 MPa (ultimate tensile strength). The strength improvement can be attributed to grain refinement, this was observed as refined beta grains which nucleated within the coarse laths of HDH treated samples. Notwithstanding that simulated cast Ti-6Al-4V has a higher ultimate tensile strength (930 MPa) than cast Ti-6Al-4V (860 MPa).⁹⁶ The HDH treatment (HDH 750) improved the ultimate tensile strength from 930 MPa to 1030 MPa, and this is 100 MPa above wrought Ti-6Al-4V.⁹⁵ Simulated cast Ti-6Al-4V has a comparable yield strength (760 MPa) to cast Ti-6Al-4V (758 MPa). The HDH treatment (HDH 750) improved the yield strength from 760 MPa to a level that is comparable to the wrought Ti-6Al-4V standard (830 MPa).⁹⁵

5.6.3 HDH treatment and tensile ductility

Hydrogenation-dehydrogenation (HDH) treatment also deters tensile ductility at dehydrogenation temperatures below 750°C. The ductility loss is up to 75% at the lowest dehydrogenation temperature 675°C and it decreases to 67% at 700°C and 28% at 725°C. The

loss in ductility is not caused by hydrogen embrittlement. Even though it is possible that an infinitesimal hydrogen concentration can be retained in the 675°C dehydrogenated sample. This infinitesimal concentration would not be sufficient to stabilise hydride phase nor embrittle the sample. Therefore, the ductility loss is caused by Ti_3Al precipitates which are retained in the microstructure after hydrogen escape. The 3 hour dehydrogenation at 675°C does not support sufficient Al diffusion to significantly dissolve the Al rich clusters within the HCP phase. Therefore, this retains an extensive degree of Al enrichment of up to 26 at.%Al which stabilises Ti_3Al in the HDH 675 sample.

5.6.4 Microstructure recombination at the 675°C-725°C dehydrogenation temperatures

The 675°C dehydrogenated microstructure is partially recombined, the degree of recombination increases with increasing dehydrogenation temperature from 675°C to 725°C. The HDH 675 sample has the least ductility, crack trajectories in its microstructure show that Ti_3Al provides crack paths which have low resistance to crack propagation (thus reduce ductility). The degree of ductility loss decreases with increasing dehydrogenation temperature from 675°C to 725°C. This indicates an increasing degree of microstructure recombination which is marked by a decreasing volume fraction of Ti_3Al precipitates. The latter is confirmed by a decreasing intensity of Ti_3Al sub-peaks in the XRD spectra of HDH 675 to HDH 725 treated Ti-6Al-4V.

5.6.5 Microstructure recombination at the 750°C dehydrogenation temperature

The 750°C dehydrogenated microstructure is significantly recombined. The HDH 750 sample has full ductility and this indicates significant Ti_3Al dissolution. However, EDS analysis of the 750°C dehydrogenated microstructure still shows some Al rich clusters (albeit a significantly reduced volume fraction) in the HCP phase. This indicates that the 3 hour dehydrogenation at 750°C does not fully homogenise the Al composition in hydride partitioned microstructures. However, it supports extensive Al diffusion which significantly dissolves Al rich clusters to extents that restore full ductility. The significantly reduced volume fraction of retained Al rich clusters in a 750°C dehydrogenated microstructure was also observed in tempered martensite. The lack or presence of Ti_3Al precipitates in these retained clusters is addressed using atomic resolution TEM in **Chapter 6**.

CHAPTER 6: THE CONTRIBUTION OF HYDROGEN TO THE EVOLUTION AND THE TENSILE PERFORMANCE OF TEMPERED MARTENSITE

Chapter 5 showed the effect of hydrogen promoted Ti_3Al precipitates on ductility. It also showed that increasing the dehydrogenation temperature from 675°C to 750°C significantly dissolved Ti_3Al to extents that recovered full ductility. **Chapter 6** evaluates the tensile performance of hydrogen tempered and non-hydrogen tempered martensite to highlight the contribution of hydrogen to ductility loss. **Chapter 6** engages with the fact that overaging (for at least 200 hours) can also precipitate Ti_3Al in non-hydrogenated Ti-6Al-4V. Therefore **Chapter 6** compares microstructure evolution in hydrogen tempered and non-hydrogen tempered martensite to highlight hydrogen's influence in promoting Ti_3Al precipitation at short aging times (3 hours).

Thermohydrogen processing (THP) consists of four steps: hydrogenation of simulated cast Ti-6Al-4V to alloy 20 at.%H, solution treatment (at 900°C for 1 hour), aging (at 580°C for 3 hours) and dehydrogenation (at 675°C or 750°C for 3 hours). A control heat treatment was similarly performed on non-hydrogenated Ti-6Al-4V which was solution treated and quenched at 1080°C (above beta transus). Microstructure evolution was characterised by: electron backscatter diffraction (EBSD), transmission Kikuchi diffraction (TKD), energy dispersive spectroscopy (EDS), selected area diffraction (SAD) and atomic resolution STEM.

Chapter 6 concludes that THP treatment improves the yield strength (YS) and the ultimate tensile strength (UTS) by approximately 130 MPa and 142 MPa respectively but it decreases the ductility by 60% at 675°C . Alloyed hydrogen contributes 40 MPa (YS) and 54 MPa (UTS) to the strength increase and 30% to the ductility loss in 675°C dehydrogenated martensite. Hydrogen contributes through combined effects from hydrogen promoted acicular martensite formation, and hydrogen promoted Ti_3Al precipitation (which occurs within 3 hours of hydrogen tempering). Hydrogen tempering stabilises nanobanded hydrides within tempered martensite plates. The nanobanded hydrides partition Al to neighbouring nanobands where the consequent Al enrichment stabilises Ti_3Al . Dehydrogenating at 750°C restores a net 20% ductility that is attributed to Ti_3Al dissolution.

6.1 Microstructure and tensile property relationships of tempered martensite which was vacuum annealed or dehydrogenated at 675°C

Figure 6.1 compares the tensile performance of hydrogen tempered and non-hydrogen tempered martensite that was dehydrogenated or vacuum annealed at 675°C to the benchmark tensile properties of simulated cast Ti-6Al-4V. The outlined samples were beta solution treated or annealed (for 1 hour), tempered or aged (for 3 hours) and dehydrogenated or vacuum annealed (for 3 hours):

- **Control 1080-580-675:** Non-hydrogenated, solution treated and quenched at 1080°C, aged at 580°C and vacuum annealed at 675°C.
- **Control 900-580-675:** Non-hydrogenated, annealed and quenched at 900°C, aged at 580°C and vacuum annealed at 675°C.
- **THP 900-580-675:** Hydrogenated, solution treated and quenched at 900°C, aged at 580°C and dehydrogenated at 675°C.

For ease of reference, tensile performance data were extracted from **Figure 6.1** and presented in **Table 6.1**, where it is compared to the American society for testing and materials (ASTM) performance requirements for cast Ti-6Al-4V (ASTM F1108-14).⁹⁶ **Figure 6.1** and **Table 6.1** show that simulated cast Ti-6Al-4V has a yield strength (YS) of 760 MPa, an ultimate tensile strength (UTS) of 930 MPa and 10% ductility. The tensile performance of simulated cast Ti-6Al-4V meets the performance requirements for Ti-6Al-4V castings which are stipulated in the ASTM F1108–14 standard.⁹⁶

Heat treating simulated cast Ti-6Al-4V under the control 1080-580-675 treatment increased the yield strength by 200 MPa (760 to 960) MPa and the ultimate tensile strength by 175 MPa (930 to 1105) MPa. It also caused a 50% ductility loss from 10% to 5% elongation. Heat treating simulated cast Ti-6Al-4V under the THP 900-580-675 treatment increased the yield strength by 130 MPa (760 to 890) MPa and the ultimate tensile strength by 142 MPa (930 to 1072) MPa. It also caused a 60% ductility loss from 10% to 4% elongation. The tensile strength and ductility loss typically increases with increasing quenching temperature.⁹⁹ However, in this instance the 1080°C quenched and 900°C quenched samples have relatively similar tensile performance. This shows that martensite formation and tempering dominates the tensile performance over the contribution from alloyed hydrogen.

The contribution of hydrogen to the observed strength increase and ductility loss was evaluated by comparing the THP 900-580-675 treatment to its non-hydrogenated counterpart. Tempering non-hydrogenated Ti-6Al-4V which was quenched at 900°C (control 900-580-675) increased the yield strength by 90 MPa (760 to 850) MPa and the ultimate tensile strength by 88 MPa (930 to 1018) MPa. It also decreased the ductility by up to 30% from 10% to 8±1% elongation. Therefore alloyed hydrogen contributed 40 MPa (130-90) MPa to the YS increase, 54 MPa (142-88) MPa to the UTS increase and 30% to the ductility loss that is observed in 675°C dehydrogenated martensite. The contribution of hydrogen emanates from hydrogen promoted acicular martensite formation and Ti₃Al precipitation.

Table 6. 1: Tensile performance of simulated cast, hydrogen tempered and non-hydrogen tempered martensite compared to the ASTM F1108-14 standard for Ti-6Al-4V castings.

Heat treatment	YS (MPa)	UTS (MPa)	Elongation (%)
Control 1080-580-675	960	1105	5
THP 900-580-675	890	1072	4
Control 900-580-675	830-850	988-1018	8±1
Sim. cast	760	930	10
ASTM F1108-14 ⁹⁶	758	860	8

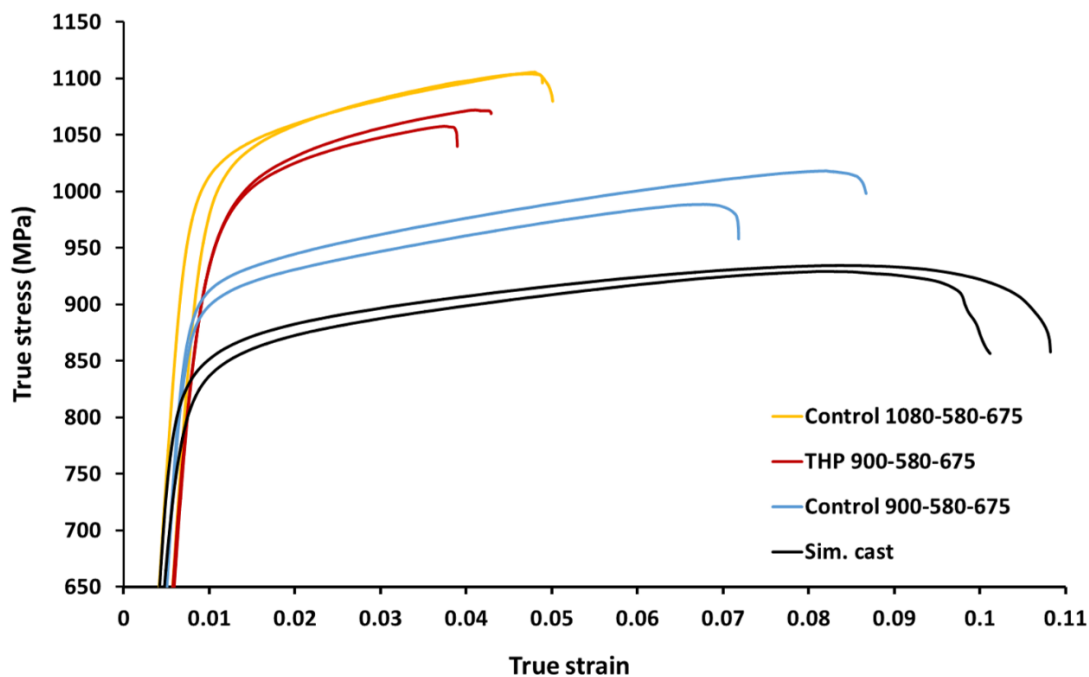


Figure 6. 1: The tensile performance of simulated cast, hydrogen tempered (THP 900-580-675) and non-hydrogen tempered Ti-6Al-4V (control 1080-580-675 and control 900-580-675) which was dehydrogenated or vacuum annealed at 675°C.

The morphology of tempered Ti-6Al-4V samples supports the observed differences in tensile performance. **Figure 6.2 a-h)** shows simulated cast Ti-6Al-4V (a-b) and the tempered microstructures; control 1080-580-675 (c-d), control 900-580-675 (e-f) and THP 900-580-675 (g-h). Simulated cast Ti-6Al-4V has a coarse Widmanstätten morphology which formed when slow cooling past the 1050°C beta transus. Quenching non-hydrogenated Ti-6Al-4V at 1080°C formed the acicular martensite morphology. Quenching non-hydrogenated Ti-6Al-4V at 900°C formed the fine Widmanstätten morphology. The 900°C quench refined Widmanstätten lamellae by eliminating the lamellae coarsening which occurs during slow cooling. Quenching hydrogenated Ti-6Al-4V at 900°C caused the acicular plate martensite transformation because 20 at.% alloyed hydrogen reduces the beta transus below 900°C.⁴² This resulted in hydrogen promoted acicular martensite formation.

The 90 MPa yield strength increase that is observed in the control 900-580-675 sample is caused by Widmanstätten lamellae refinement. Reheating non-hydrogenated Ti-6Al-4V to the 900°C transforms some primary alpha to beta phase. Subsequently quenching to room temperature transforms the nucleated beta to secondary alpha phase. The fast cooling rate (quenching) enables secondary alpha to retain fine Widmanstätten lamellae. Minimal coarsening occurred during subsequent tempering and this retained the fine lamellae. The 200 MPa or 130 MPa yield strength increase that is observed in the control 1080-580-675 or THP 900-580-675 treatments is caused by martensite hardening and the grain refinement which occurs during martensite tempering. The latter nucleates refined equilibrium phases that improve strength.¹⁰⁰

The relationship between morphology and tensile ductility is articulated in literature. Lamellar and acicular microstructures are less ductile because their linear configuration provides linear crack paths which have relatively low resistance to crack propagation.^{101, 102} This is why the Widmanstätten microstructure has lower ductility when compared to the equiaxed microstructure.¹⁰¹ It also explains why the Widmanstätten, acicular and hydrogen promoted acicular morphologies in **Figure 6.2** have 30%, 50% and 60% ductility loss respectively.

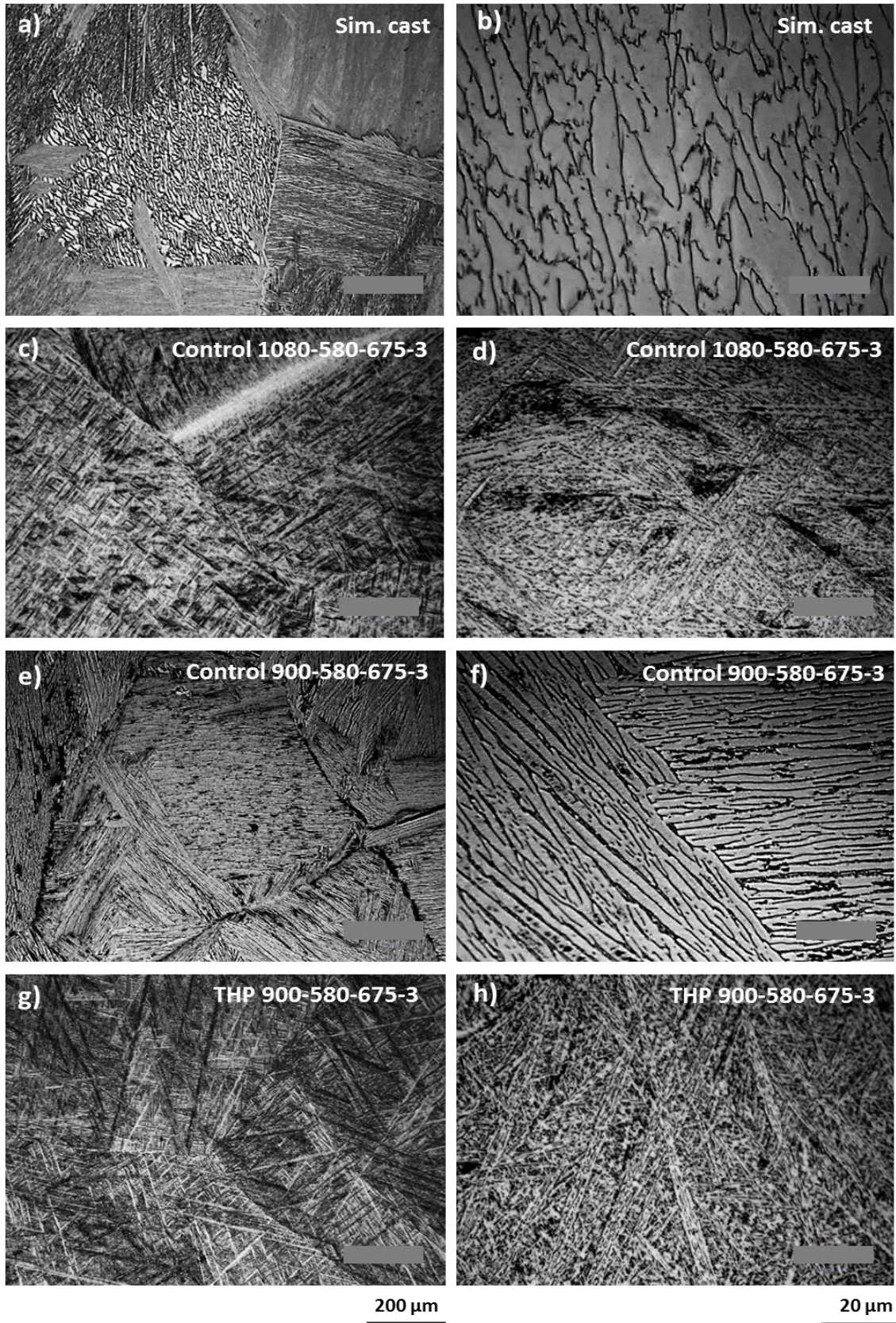


Figure 6. 2: Optical micrographs of a-b) simulated cast, b-c) control 1080-580-675, e-f) control 900-580-675, g-h) THP 900-580-675 samples showing; a-b) coarse Widmanstätten morphology, c-d) acicular morphology, e-f) fine Widmanstätten morphology and g-h) hydrogen promoted acicular morphology.

6.2 Microstructure and tensile property relationships of tempered martensite which was vacuum annealed or dehydrogenated at 750°C

Section 6.1 articulated the tensile ductility differences that are caused by varied morphologies (Widmanstätten or acicular). This work extends beyond the literature articulated morphology variance, tensile ductility relationships. It focuses on the contribution of hydrogen to the ductility difference that is observed in microstructures that have the same morphology (for instance acicular martensite). Hydrogen's contribution is eliminated after increasing the dehydrogenation temperature from 675°C to 750°C.

Figure 6.3 a-d) compares the morphologies of Ti-6Al-4V martensite which was tempered in the absence (control 1080-580-750) or presence (THP 900-580-750) of hydrogen and subsequently vacuum annealed or dehydrogenated at 750°C:

- **Control 1080-580-750.** Non-hydrogenated, solution treated at 1080°C and quenched, aged at 580°C and vacuum annealed at 750°C.
- **THP 900-580-750.** Hydrogenated, solution treated at 900°C and quenched, aged at 580°C and dehydrogenated at 750°C.

Figure 6.3 a-d) shows that dehydrogenating or vacuum annealing at 750°C does not significantly change the morphology relative to dehydrogenating or vacuum annealing at 675°C. The morphology of tempered martensite (control 1080-580-750, THP 900-580-750) remains acicular after vacuum annealing or dehydrogenating at 750°C. This is because 750°C is below the beta transus temperature, thus it does not promote significant new beta (β) formation and hence Widmanstätten growth during cooling. Therefore, dehydrogenating or vacuum annealing at 750°C primarily coarsens the acicular morphology.

Figures 6.4 and 6.5 show the effect of increasing the vacuum annealing or dehydrogenation temperature from 675°C to 750°C on the tensile performance of tempered martensite. For ease of reference the yield strength (YS), ultimate tensile strength (UTS) and elongation (%) values from **Figures 6.4 and 6.5** are given in **Table 6.2** and compared to the ASTM performance standard for Ti-6Al-4V castings (ASTM F1108-14).⁹⁶

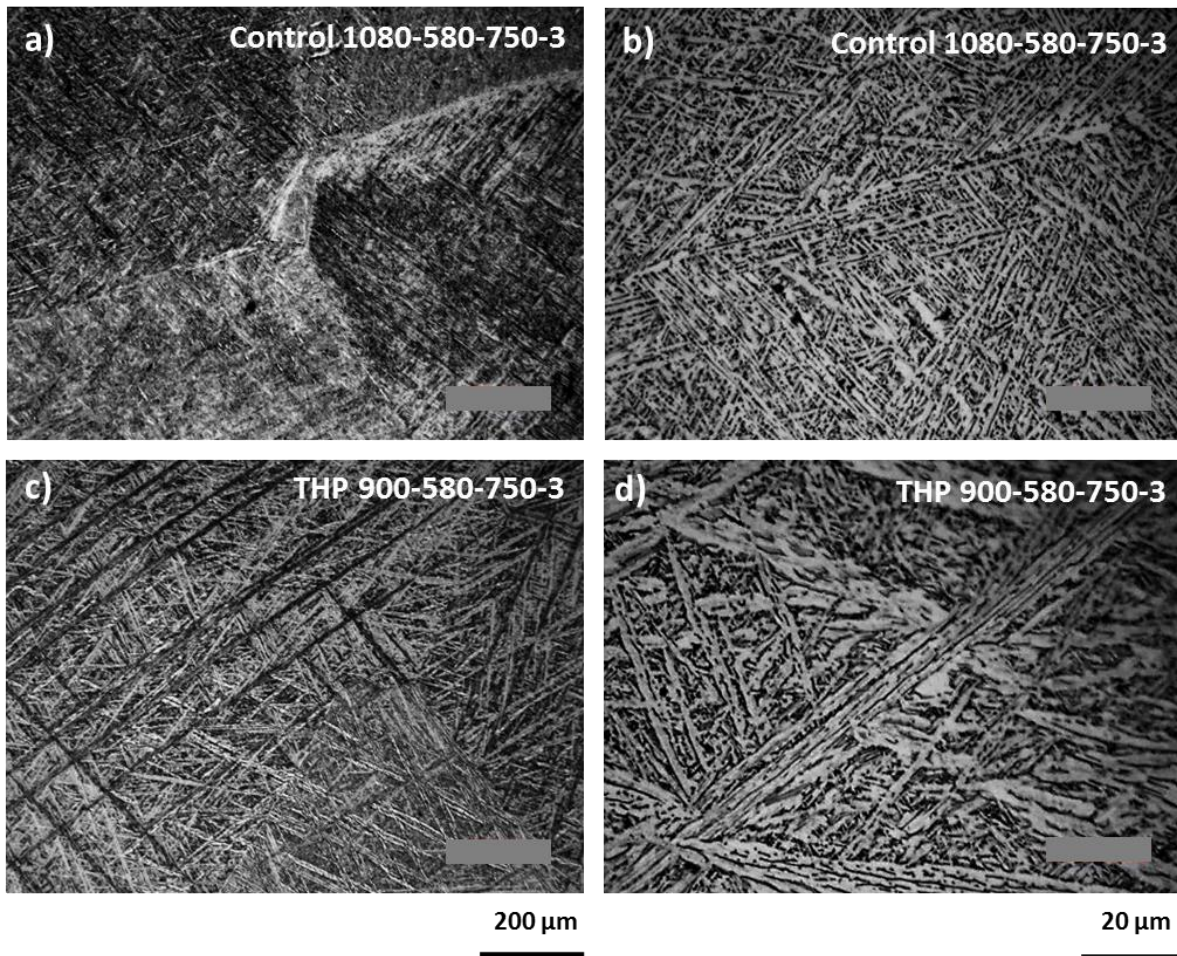


Figure 6. 3: Optical micrographs of a-b) control 1080-580-750, c-d) THP 900-580-750 samples showing all acicular morphologies after dehydrogenating at 750°C. Increasing the dehydrogenation temperature from 675°C to 750°C does not change the acicular morphology.

Figure 6.4 and **Table 6.2** show that increasing the vacuum annealing temperature from 675°C to 750°C decreases the strength of non-hydrogen tempered martensite. The YS decreases by 70 MPa (960-890) MPa and the UTS decreases by 35 MPa (1105-1070) MPa. Increasing the vacuum annealing temperature also recovers 12% ductility from 5% to 6.2% elongation.

Similarly, **Figure 6.5** and **Table 6.2** show that increasing the dehydrogenation temperature from 675°C to 750°C decreases the strength of hydrogen tempered martensite. The YS decreases by 70 MPa (890-820) MPa and the UTS decreases by 32 MPa (1072-1040) MPa. Increasing the dehydrogenation temperature also recovers about 32% ductility from 3.8% to 7% elongation.

The strength loss at 750°C is caused by martensite softening. The softening resulted from acicular plate coarsening at 750°C; this can be observed after comparing **Figure 6.2 d, h)** to **Figure 6.3 b, d)**. The degree of martensite softening was similar in hydrogen tempered and non-hydrogen tempered martensite because they both had similar strength losses of 70 MPa (YS) and approximately 30 MPa (UTS). Notwithstanding the softening, the tempered martensite strength still exceeds the ASTM F1108-14 standard strength requirements.

Figures 6.4 and **6.5** show that vacuum annealing or dehydrogenating at 750°C also recovered ductility. Hydrogen tempered martensite recovered more ductility when compared to non-hydrogen tempered martensite. In **Figure 6.4**, non-hydrogen tempered martensite recovered 12% ductility from approximately 0.05 to 0.062 strain. In comparison, **Figure 6.5** shows that hydrogen tempered martensite recovered 32% ductility from approximately 0.038 to 0.07 strain. However, this ductility is below the ASTM F1108-14 requirement.

The 12% ductility that is recovered in non-hydrogen tempered martensite is associated with the 750°C martensite softening. Offsetting the 10% leaves a net 20% recovered ductility that is unique to hydrogen tempered martensite. The net 20% recovered ductility indicates that hydrogen tempered martensite has additional modes of embrittlement. This also explains why the THP 900-580-675 sample has 10% lower ductility (0.04 strain) when compared to the control 1080-580-675 sample (0.05 strain). Ideally, the former would be expected to be more ductile because it has lower strength than the latter. The acicular morphology embrittlement intersects with added contributions from hydrogen promoted microstructure evolution to deplete the ductility of hydrogen tempered martensite.

Table 6. 2: *The effect of increasing the vacuum annealing or dehydrogenation temperature from 675°C to 750°C on the tensile performance of tempered martensite.*

Heat treatment	YS (MPa)	UTS (MPa)	Elongation (%)
Control 1080-580-675	960	1105	5
Control 1080-580-750	890	1070	5.8±0.4
THP 900-580-675	890	1072	4±0.2
THP 900-580-750	820	1040	7
ASTM F1108 – 14 ⁹⁶	758	860	8

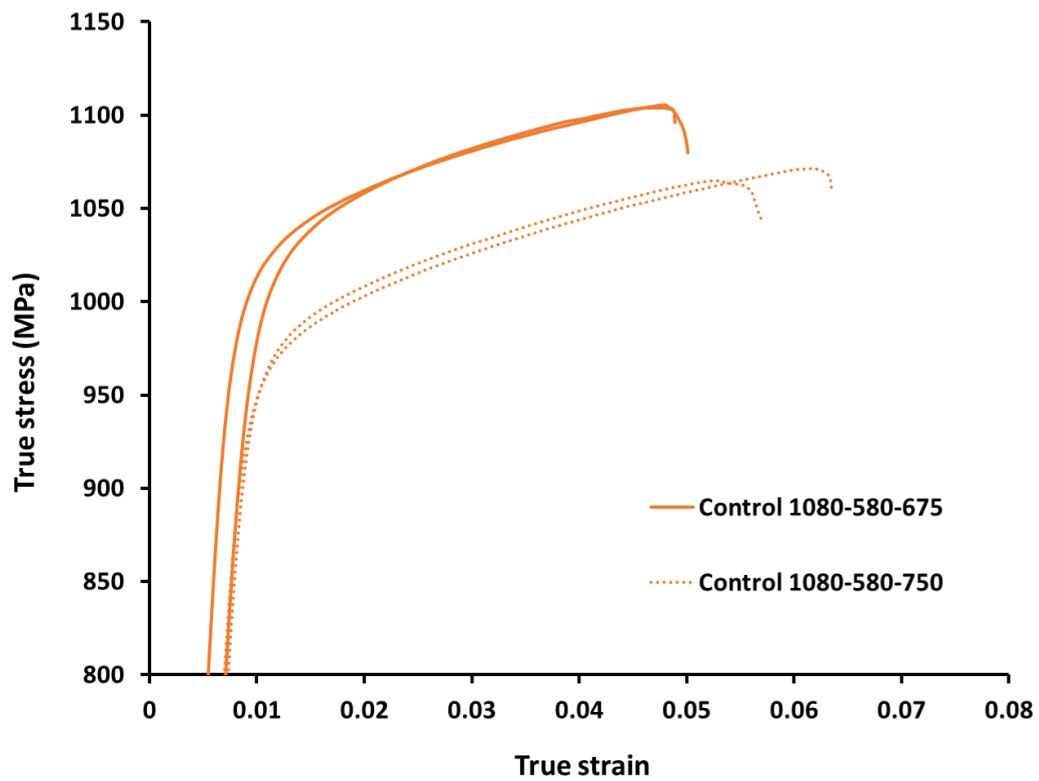


Figure 6. 4: Non-hydrogen tempered Ti-6Al-4V martensite showing 12% recovered ductility after increasing vacuum annealing temperature from 675°C to 750°C.

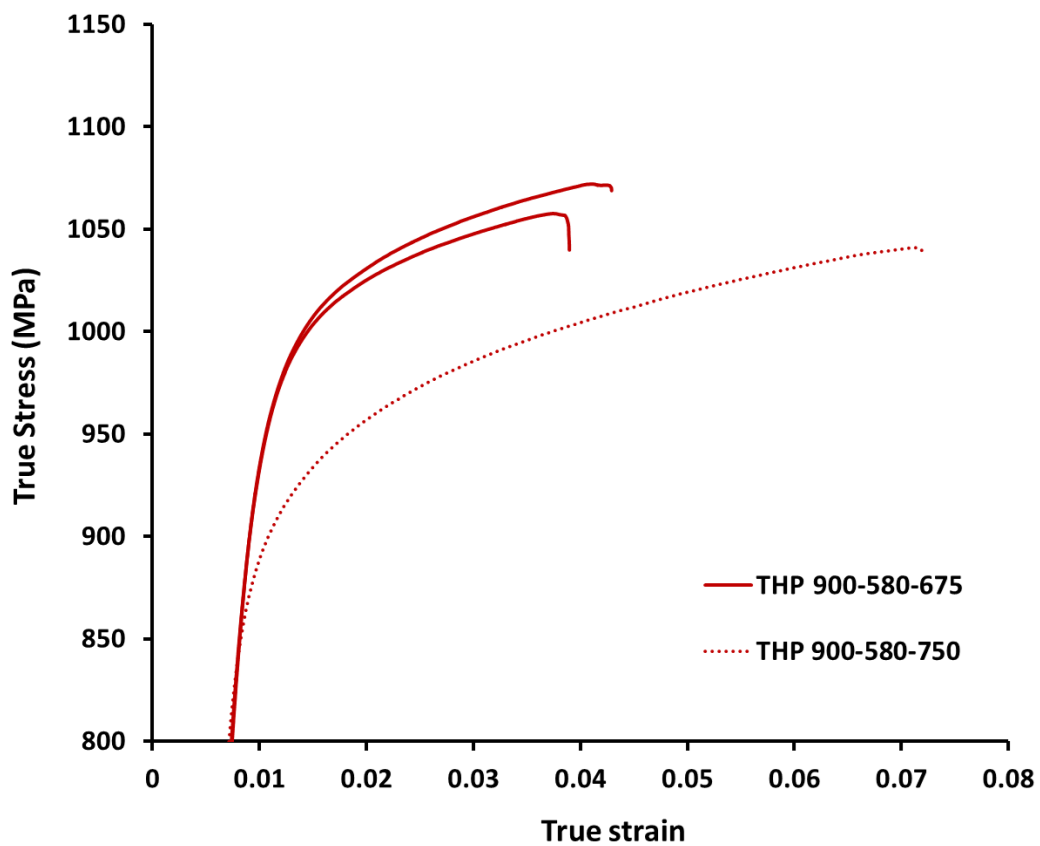


Figure 6. 5: Hydrogen tempered Ti-6Al-4V martensite showing 32% recovered ductility after increasing the dehydrogenation temperature from 675°C to 750°C.

6.3 The contribution of hydrogen to tempered martensite evolution

Overaging for at least 200 hours can precipitate Ti_3Al in non-hydrogenated Ti-6Al-4V. However, the existing overaging investigations have been primarily performed on equilibrium Ti-6Al-4V microstructures. Therefore it is not clear if overaging is equally required to precipitate Ti_3Al in non-hydrogenated martensite.

Table 6.3 shows a collection of studies on aged Ti-6Al-4V; it relates the reported instances of Ti_3Al precipitation to the starting microstructure, aging conditions and hydrogen treatment.

Table 6.3 shows that Ti_3Al precipitates in non-hydrogenated, equilibrium microstructures (Widmanstätten, equiaxed and bimodal) which were overaged for a minimum of 200 hours between 500°C and 600°C.^{101, 103-105} However, it is not clear whether long overaging times are equally necessary to precipitate Ti_3Al in non-hydrogenated martensite.

Table 6.3 also shows that non-hydrogenated martensite has been aged in several studies for up to 24 hours,¹⁰⁶⁻¹⁰⁹ but Ti_3Al precipitates were not reported. This means one of two things: firstly Ti_3Al was not present and thus not reported, or secondly Ti_3Al was present but it was not identified because the studies characterised the microstructure using optical and scanning electron microscopy. The lack of clarity worsens when Ti_3Al precipitates are also not reported in hydrogenated martensite that was aged up to 100 hours.^{9, 15, 16, 45}

Therefore this study is aware that Ti_3Al can precipitate in equilibrium, non-hydrogenated Ti-6Al-4V which is overaged for at least 200 hours. However, there is a gap in literature because the threshold aging conditions that precipitate Ti_3Al in non-hydrogenated martensite are not known. In the context of this study, it is crucial to know if Ti_3Al precipitates in non-hydrogenated martensite after 3 hours of aging. This will distinguish the contribution of hydrogen to the ductility loss observed in tempered martensite.

Therefore this argument raises the question;

- Does Ti_3Al precipitate in non-hydrogenated martensite after aging at 580°C for 3 hours?

Table 6. 3: A collection of studies on aged Ti-6Al-4V.

Author	Microstructure	at.%H	Aging conditions		Ti ₃ Al	Technique
			Temp (°C)	Time (hours)		
Carreon et al. ¹⁰³	Widmanstätten, Equiaxed	-	545	Up to 576	✓	SEM
Wu et al. ¹⁰⁴	Equiaxed	-	500	840	✓	TEM, APT
Lee et al. ¹⁰¹	Widmanstätten, Equiaxed, Bimodal	-	545	200	✓	SEM, TEM-SAD
Lee and Lee ¹⁰⁵	Bimodal	-	545	200, 300	✓	SEM
Xu et al. ¹⁰⁶	Martensite	-	400, 540, 800	2	x	SEM-BSE
Mur et al. ¹⁰⁷	Martensite	-	400, 600, 700, 800	up to 2	x	SEM
Gheysarian and Abbasi ¹⁰⁸	Martensite	-	550	4	x	OM
Oh et al. ¹⁰⁹	Martensite	-	550	24	x	SEM
Qazi et al. ¹⁵	Martensite	10, 20, 30	530-780	up to 100	x	TEM-SAD
Qazi et al. ¹⁶	Martensite	10, 20, 30	530-780	up to 64	x	OM, TEM-SAD
Sun et al. ⁴⁵	Martensite	17, 27	500, 700	up to 10	x	TEM-BF
Yoshimura et al. ⁹	Martensite	10, 20, 25, 30	500	8	x	SEM, TEM-BF

at.%H - Atomic percent alloyed hydrogen; (✓) - Ti₃Al reported; (x) - Ti₃Al not reported; **SEM-BSE** - Scanning electron microscope, backscattered electron analysis; **OM** - Optical microscopy; **TEM-SAD** - Transmission electron microscope, selected area diffraction analysis; **TEM-BF** -TEM bright field; **APT** - Atomic probe tomography

Section 6.3 evaluates if Ti_3Al precipitates in non-hydrogenated martensite after aging at 580°C for 3 hours in order to unambiguously confirm the extent of hydrogen's contribution to Ti_3Al precipitation in tempered martensite. Therefore **Section 6.3** compares microstructure evolution in hydrogen tempered martensite and non-hydrogen tempered martensite. This comparison is done on samples that were extracted at the quenched, aged and dehydrogenated or vacuum annealed stages of the martensite tempering treatment. The extracted samples were characterised at high resolution using EBSD, TKD and HRTEM and atomic resolution TEM.

6.3.1 EBSD analysis of as-quenched martensite in hydrogenated and non-hydrogenated Ti-6Al-4V

Martensite samples were quenched above the beta transus temperature; this was at 900°C for hydrogenated Ti-6Al-4V because the alloyed 20 at.%H reduces the beta transus below 900°C .⁴² In comparison, this was 1080°C for non-hydrogenated Ti-6Al-4V because the beta transus temperature is 1050°C .⁴² **Figures 6.6 a-c)** and **6.7 a-c)** compare a) EBSD phase maps and EDS composition maps of b) Al, c) V in hydrogenated (**Figure 6.6 a-c)** and non-hydrogenated (**Figure 6.7 a-c)** Ti-6Al-4V martensite.

Figure 6.6 a) shows that the hydrogenated, solution treated and quenched sample underwent a partial BCC to HCP acicular plate martensite transformation during quenching. This is because alloyed hydrogen stabilised some of the high temperature BCC phase as a metastable phase at room temperature. **Figures 6.6 b, c)** show that the partial martensite transformation was diffusionless because there is no variation in aluminium (Al), vanadium (V) composition between the HCP acicular martensite plates and the hydrogen stabilised BCC phase.

In comparison, **Figure 6.7 a)** shows that the non-hydrogenated, solution treated and quenched sample has no hydrogen stabilised BCC phase. Therefore it underwent a full BCC to HCP acicular plate martensite transformation during quenching. Its complementary EDS analysis in **Figure 6.7 b, c)** also shows no variation in Al, V composition and confirms that the non-hydrogenated sample underwent a diffusionless BCC to HCP acicular plate martensite transformation.

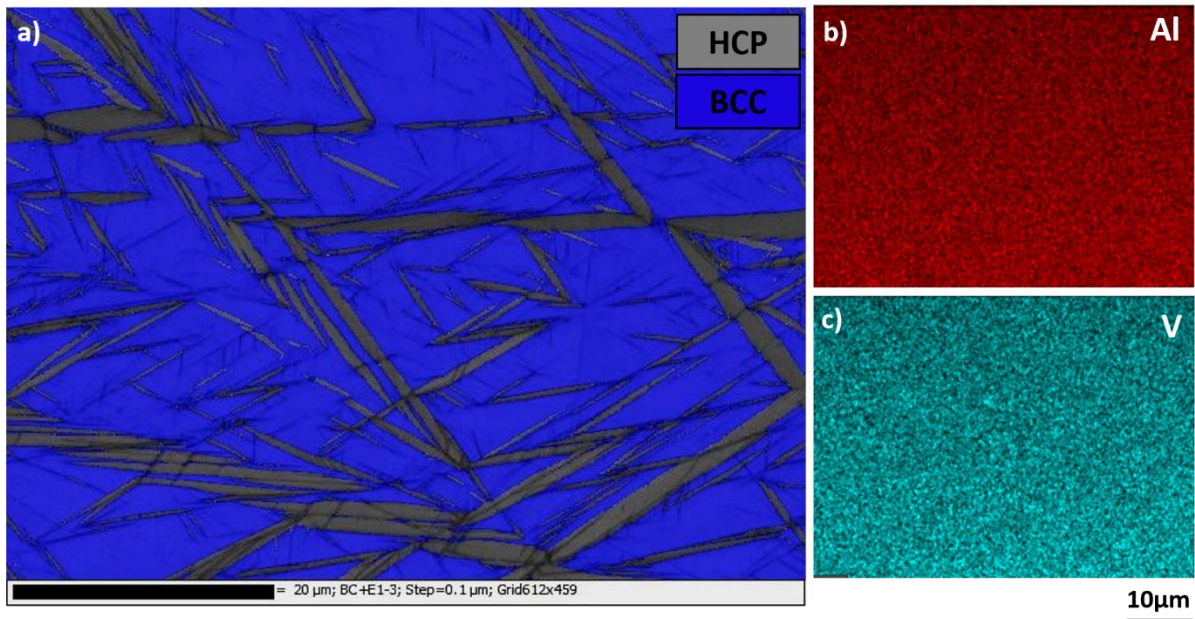


Figure 6. 6: Complementary a) EBSD phase map and EDS b) Al, c) V maps of 20 at.% hydrogenated, solution treated (at 900°C), and quenched Ti-6Al-4V. Image a) shows that the quenched microstructure has HCP (grey) acicular martensite plates and a hydrogen stabilised BCC (blue) interplate region. Images b) and c) show no variation in Al, V composition in the HCP and BCC phases which confirms a diffusionless BCC to HCP martensite transformation.

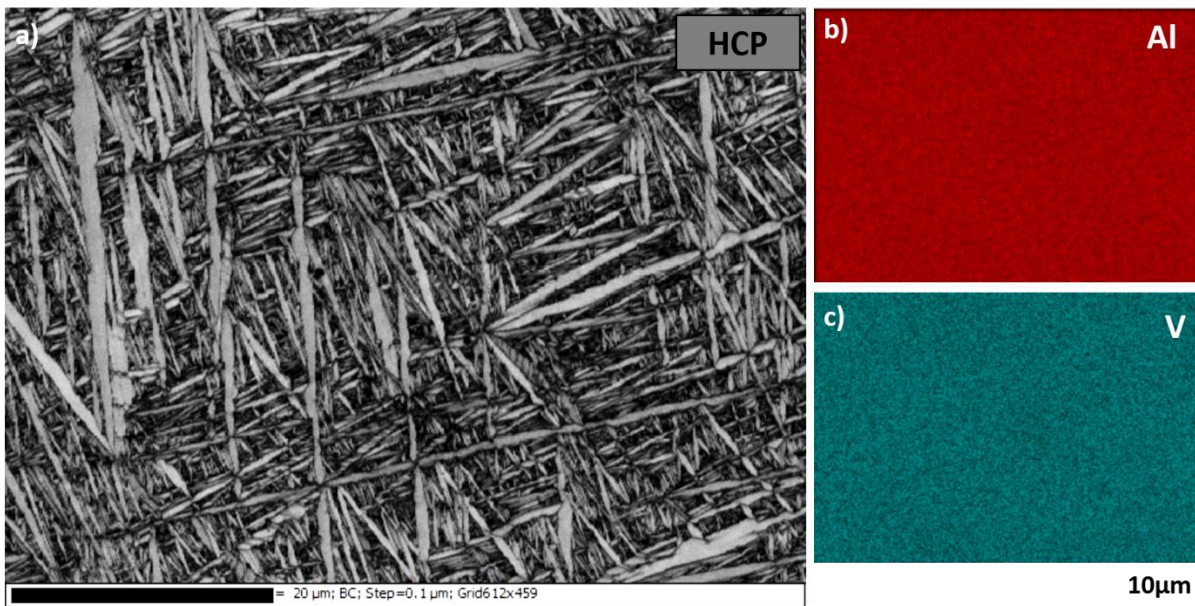


Figure 6. 7: Complementary a) EBSD phase map and EDS b) Al, c) V maps of non-hydrogenated, solution treated (at 1080°C), and quenched Ti-6Al-4V. Image a) shows that the quenched microstructure has HCP (grey) acicular martensite plates and no indexed BCC phase. Images b) and c) show no variation in Al, V composition across the HCP and BCC phases which confirms a diffusionless BCC to HCP martensitic transformation.

6.3.2 EBSD analysis of hydrogen tempered and non-hydrogen tempered martensite

Martensitic samples were reheated to 580°C, hydrogen tempered or non-hydrogen tempered for 3 hours and quenched. **Figures 6.8 a-c)** and **6.9 a-c)** compare a) EBSD phase maps and EDS composition maps of b) Al, c) V in hydrogen tempered (**Figure 6.8 a-c)** and non-hydrogen tempered (**Figure 6.9 a-c)** martensite.

Figure 6.8 a) shows that hydrogen tempered martensite has HCP tempered martensite plates, some BCC phase and FCC, FCT hydrides. Reheating to aging temperature and subsequently soaking at aging temperature decomposed most of the hydrogen stabilised BCC phase to nucleate HCP phase. The BCC to HCP transformation saturated the HCP phase with hydrogen, because the BCC phase dissolves more hydrogen (up to 45 at.%H)^{43, 51} when compared to the HCP phase which dissolves up to 8 at.%H.^{8, 43} Hydrogen saturated alpha ultimately transformed to FCC (Ti-H₂) or FCT (Ti-H) hydride phase. Hydrides precipitated in the interplate region as fine hydrides (FH) or linear hydrides (LH), and within tempered martensite plates as nanobanded hydrides (NH). The white arrows in **Figure 6.8 a)** show nanobanded hydrides within tempered martensite plates. **Figure 6.8 b, c)** shows that martensite decomposition occurred through a diffusion controlled partitioning of Al and V. They also confirm that hydride nanobands are rich in V and lean in Al, whilst their neighbouring nanobands are rich in Al. This indicates that hydride nanobands partitioned Al from its Ti-Al couple. The partitioned Al enriched neighbouring nanobands with Al (as discussed in **Chapter 4**).

In comparison, non-hydrogen tempered martensite in **Figure 6.9 a)** only has HCP phase. This is expected because the 580°C volume fraction of BCC phase in non-hydrogenated Ti-6Al-4V is less than 10%.⁸⁹ **Figure 6.9 b, c)** shows that non-hydrogen tempered martensite has no significant variation in Al, V composition. This is also expected because only HCP phase is indexed in the field of view. Non-hydrogen tempered martensite has no visible nanobands or partitioning of Al, V within tempered martensite plates.

The contribution of hydrogen to tempered martensite evolution was subsequently evaluated using high resolution and atomic resolution transmission electron microscopy. Electron transparent samples were extracted from hydrogen tempered and non-hydrogen tempered samples as described in **Section 6.4**.

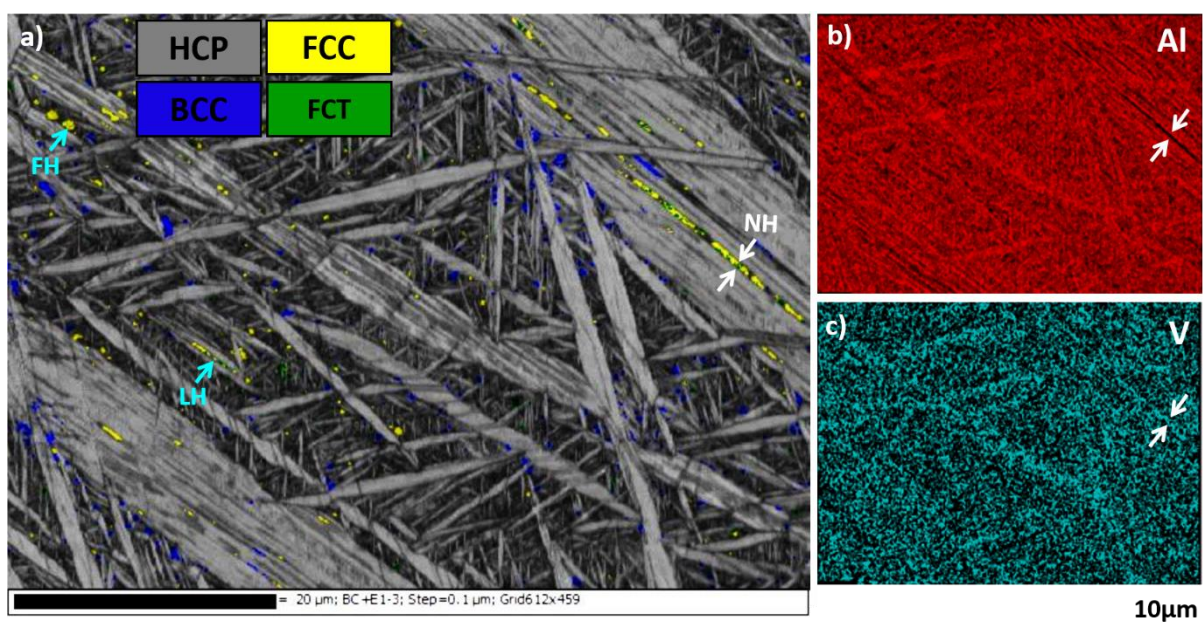


Figure 6. 8: Complementary a) EBSD phase map and EDS b) Al, c) V maps of 20 at.% hydrogenated, solution treated (at 900°C), quenched and aged or tempered (at 580°C) Ti-6Al-4V. Image a) shows that hydrogen tempered martensite has HCP (grey) tempered martensite plates, some BCC (blue) phase and FCC (yellow) and FCT (green) hydrides. Image a) highlights (in white arrows) nanobanded hydrides (NH) within acicular plates, fine hydrides (FH) and linear hydrides (LH) in the interplate region. Images b) and c) show that the nanobanded hydrides are rich in V and lean in Al.

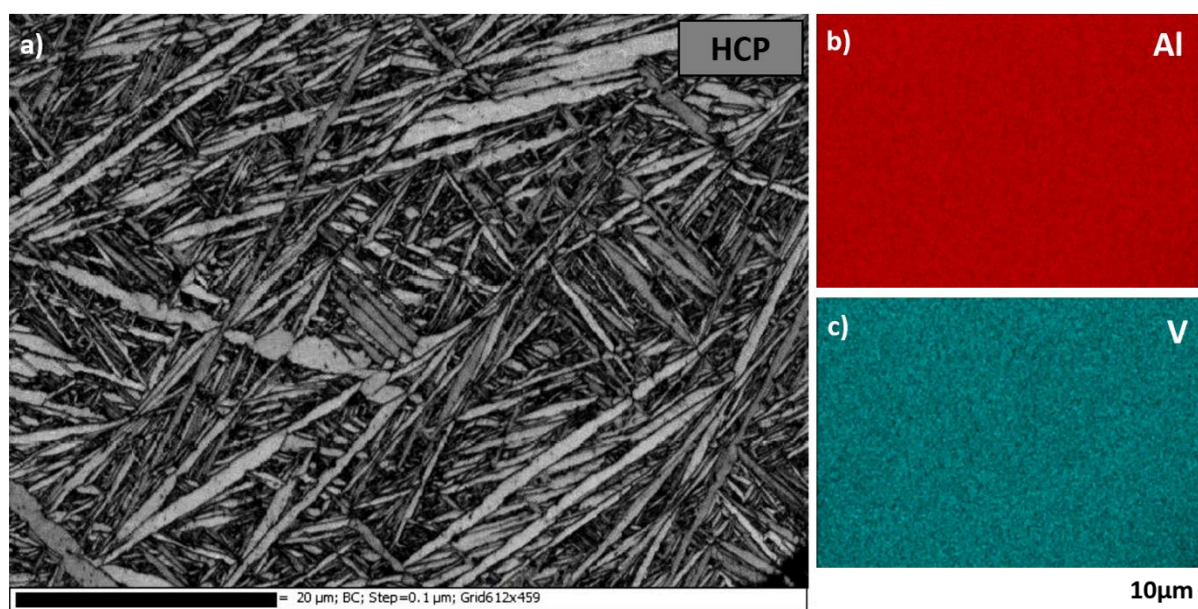


Figure 6. 9: Complementary a) EBSD phase map and EDS b) Al, c) V maps of non-hydrogenated, solution treated (at 1080°C), quenched and aged or tempered (at 580°C) Ti-6Al-4V. Image a) shows that non-hydrogen tempered martensite has HCP (grey) tempered martensite plates and no indexed BCC and hydride phases. Image a) shows that there are no nanobands within the tempered martensite plates. Images b-c) also show no significant Al, V partitioning in non-hydrogen tempered martensite.

6.4 High resolution analysis of hydrogen tempered and non-hydrogen tempered martensite

Electron transparent (100nm thick) foils were extracted from hydrogen tempered martensite at the 580°C aged, 675°C dehydrogenated, and 750°C dehydrogenated stages using a focused ion beam in the scanning electron microscope (FIB-SEM). The electron transparent foils were similarly extracted in non-hydrogen tempered martensite at the 580°C aged, 675°C vacuum annealed and 750°C vacuum annealed stages.

Figure 6.10 is a schematic diagram showing the sites of extraction for electron transparent foils. The FIB-SEM foils were extracted from: 1) regions encompassing coarse martensite plates or 2) regions spanning across martensite plates. Options 1) or 2) were determined by the width of the particular martensite plate. The electron transparent foils were subsequently analysed using complementary TKD and EDS and to characterise phase and morphology evolution within acicular HCP plates. The phase constitution and phase composition within acicular martensite plates was confirmed using the TEM.

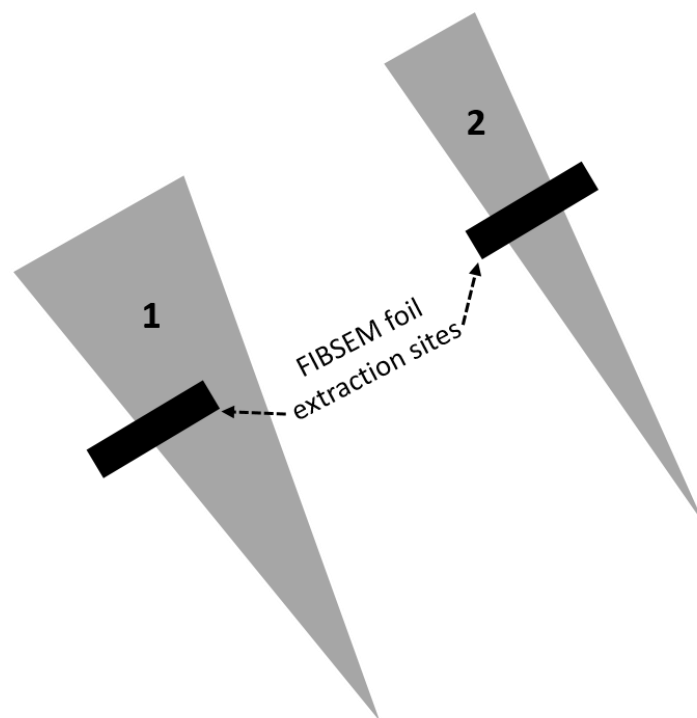


Figure 6. 10: Schematic diagram showing how FIB-SEM foils were extracted at 1) regions encompassing coarse martensite plates or 2) regions spanning across acicular martensite plates. The options 1) or 2) were determined by the width of the acicular martensite plate.

Figures 6.11 a-c) and **6.12 a-c)** compare a) TKD phase and EDS maps of b) Al, c) V in hydrogen tempered (**Figure 6.11 a-c)** and non-hydrogen tempered (**Figure 6.12 a-c)** martensite.

Bulk EBSD analysis confirmed hydride precipitates in hydrogen tempered martensite (see **Figure 6.8**). Therefore hydrides were expected in its electron transparent counterpart. However, **Figure 6.11 a)** shows that only HCP phase is indexed in hydrogen tempered martensite. This indicates that hydrogen inadvertently escaped electron transparent FIB-SEM foils after vacuum exposure. The inadvertent hydrogen escape in **Figure 6.11 a)** decomposed FCC, FCT hydrides to HCP alpha phase. This room temperature transformation had limited diffusion, and it retained the extensive Al enrichment that was caused by nanobanded hydrides within tempered martensite plates. Therefore the contribution of hydrogen could still be traced after hydrogen escape and hydride decomposition. For instance, **Figure 6.11 a)** shows characteristic V rich nanobands which were confirmed to be hydrides in the bulk sample. The V rich nanobands have neighbouring Al rich nanobands which also aligns with the observations from the bulk sample (see **Figure 6.8**).

In comparison, the TKD phase map in **Figure 6.12 a)** shows that non-hydrogen tempered martensite mostly has HCP phase and some BCC phase. There is no nanobanding within non-hydrogen tempered martensite plates. **Figure 6.12 b, c)** also shows that there is no significant Al or V enrichment in non-hydrogen tempered martensite. The latter indicates that Ti_3Al does not precipitate in non-hydrogenated martensite after aging at 580°C for 3 hours.

Elemental partitioning is a normal component of martensite decomposition. However, hydrogen intensified the degree of Al partitioning by precipitating nanobanded hydrides. The latter partitioned Al to neighbouring nanobands where the consequent Al enrichment stabilised Ti_3Al within 3 hours of aging. **Figure 6.13** shows a, c) bright field and b) HAADF STEM micrographs of hydrogen tempered martensite (see **Figure 6.11**). Selected area diffraction was performed in the nanobanded plate highlighted in image c). The complementary SAD pattern in d) confirmed Ti_3Al precipitates at a $[10\bar{1}0]$ zone axis. The absence of superlattice reflections in the simulated $[10\bar{1}0]$ alpha pattern confirms that the attained $[10\bar{1}0]$ pattern is Ti_3Al not alpha. In conclusion, Ti_3Al precipitates in hydrogen tempered martensite, but it does not precipitate in non-hydrogen tempered martensite after aging at 580°C for 3 hours.

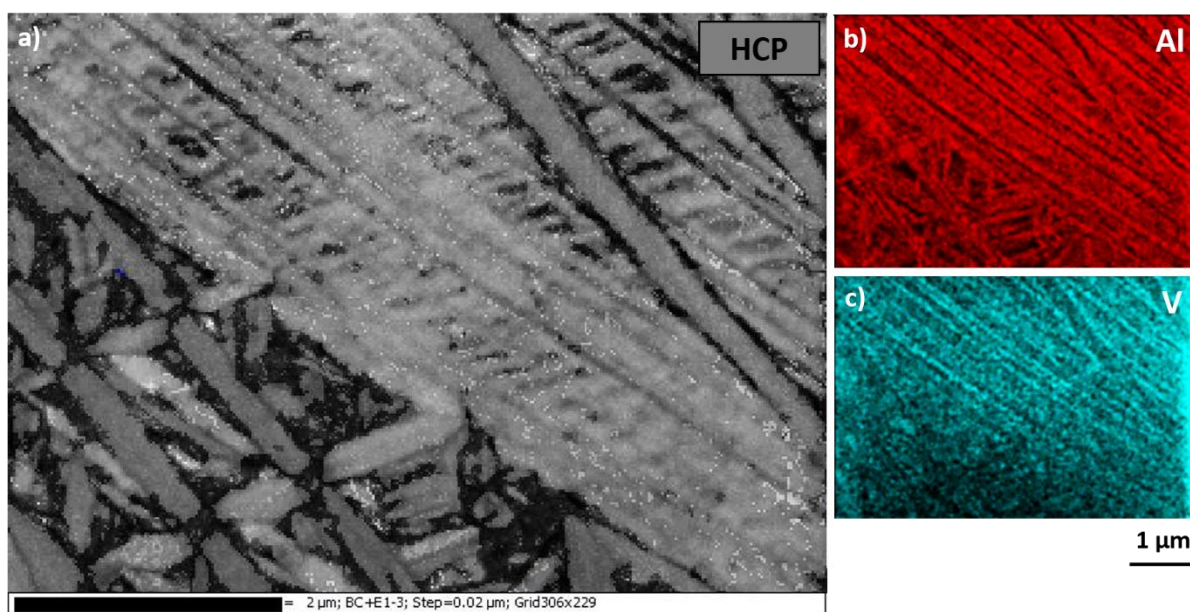


Figure 6. 11: Complementary a) TKD phase map and EDS b) Al, c) V maps of 20 at.% hydrogenated, solution treated (at 900°C), quenched and aged (at 580°C) Ti-6Al-4V. Image a) shows that hydrogen tempered martensite has HCP (grey) acicular plates and no indexed BCC and hydride phases. Images a-c) shows nanobands within acicular plates which have characteristic Al, V enrichment. Hydride precipitates were expected in the V rich nanobanded region. Hydrides are not indexed because inadvertent hydrogen escape in electron transparent samples decomposed hydrides to the indexed V rich HCP phase.

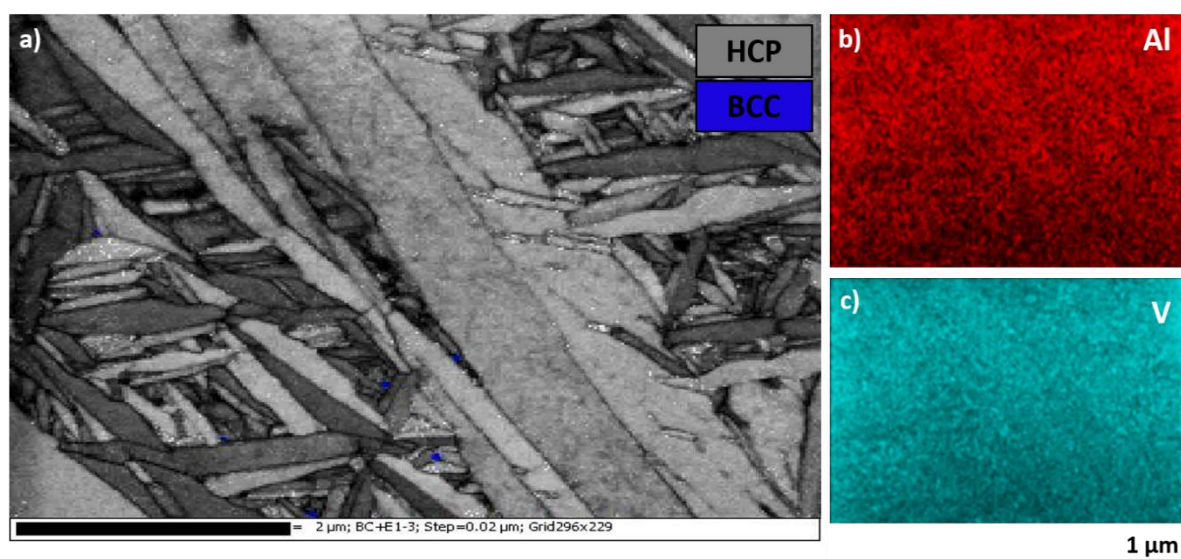


Figure 6. 12: Complementary a) TKD phase map and EDS b) Al, c) V maps of non-hydrogenated, solution treated (at 1080°C), quenched and aged (at 580°C) Ti-6Al-4V. Image a) shows that non-hydrogen tempered martensite has HCP (grey) acicular plates, some BCC (blue) and no indexed hydride phase. Image a) shows no nanobands within acicular plates. Images b) and c) also show no significant enrichment but the expected partitioning of Al and V between HCP and BCC phases.

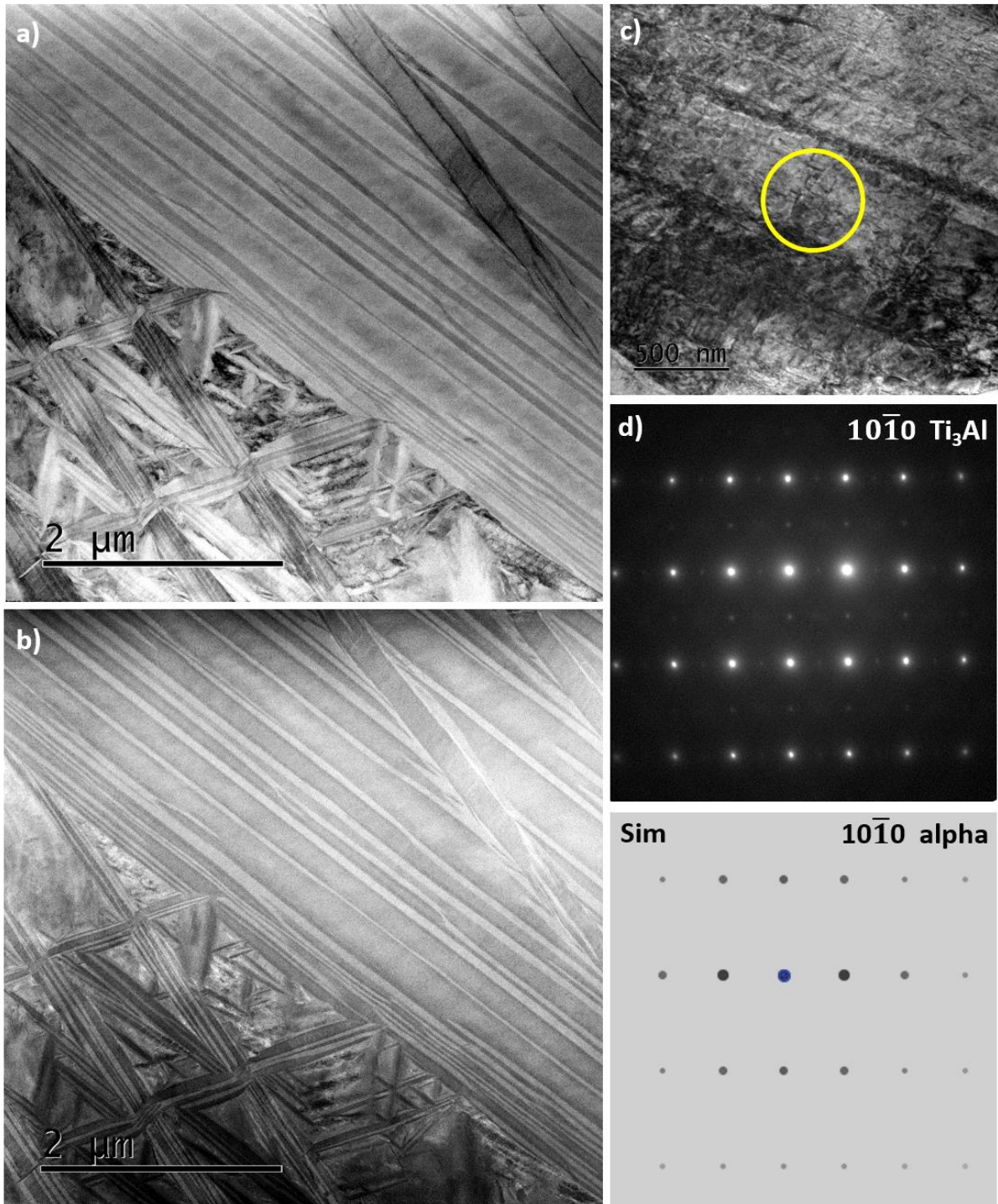


Figure 6. 13: a, c) bright field and b) HAADF STEM micrographs of 20 at.% hydrogenated, solution treated (at 900°C), quenched and aged (at 580°C) Ti-6Al-4V (see **Figure 6.11**). Selected area diffraction was performed at the nanobanded plate (highlighted in c) which confirmed d) Ti₃Al precipitates at a $[10\bar{1}0]$ zone axis. The absence of superlattice reflections in the simulated (Sim) $[10\bar{1}0]$ alpha pattern confirms that the attained $[10\bar{1}0]$ pattern is Ti₃Al not alpha. Therefore Al rich nanobands stabilised Ti₃Al precipitates within hydrogen tempered martensite plates.

6.4.1 The nanobanded morphology in hydrogen tempered martensite

The nanobanded morphology is a typical hydride morphology that occurs when hydride precipitates configure to a particular nucleation interface. It has been observed within hydrogen tempered orthorhombic martensite plates after nucleating from twin interfaces¹⁶ or stacking faults.⁵¹ It has also been observed in hydrogenated and beta decomposed Ti-6Al-4V, after nucleating from alpha grain interfaces.^{50, 51}

The current study observed the nanobanded morphology within hydrogen tempered martensite plates. Bulk EBSD data showed an alternate configuration of alpha and hydride nanobands which were characteristically enriched in Al or V respectively. Vanadium rich hydrides partition Al; this enriches neighbouring nanobands with Al and causes the periodic variation in Al and V composition that is characteristic to the nanobanded morphology.

Figure 6.14 a) shows a HAADF STEM micrograph highlighting V rich (R1) and Al rich (R2) nanobands. **Figures 6.14 b, c)** are atomic resolution HAADF STEM micrographs showing the arrangement of atomic columns in the b) V rich and c) Al rich nanobands. **Figures 6.14 d, e)** are fast Fourier transforms of the d) V rich, e) Al rich nanobands which are indexed in f).

The atomic resolution HAADF STEM of b) V rich and c) Al rich nanobands in **Figure 6.14** shows a relatively similar configuration of atomic columns. This indicates that the Al rich and V rich nanobands have the same crystal structure and crystallographic orientation. This observation is confirmed by their $[10\bar{1}0]$ zone axis Fourier transforms in d, e). The region R2 Fourier transform in image e) has additional superlattice reflections (yellow arrows) which confirm Ti_3Al precipitates in the Al rich nanoband. This indicates that the V rich nanoband was a hydride phase that partitioned Al. This consequently enriched its neighbouring nanoband with Al to critical levels that stabilised Ti_3Al precipitates. Subsequent exposure to vacuum during FIBSEM foil extraction, TKD or TEM analyses inadvertently dehydrogenated the electron transparent foil and transformed the hydrides to V rich alpha as shown in **Figure 6.11**. Consequently, the TEM analysis in **Figure 6.14** confirms nanobands as alternate HCP bands which are either V rich or Al rich.

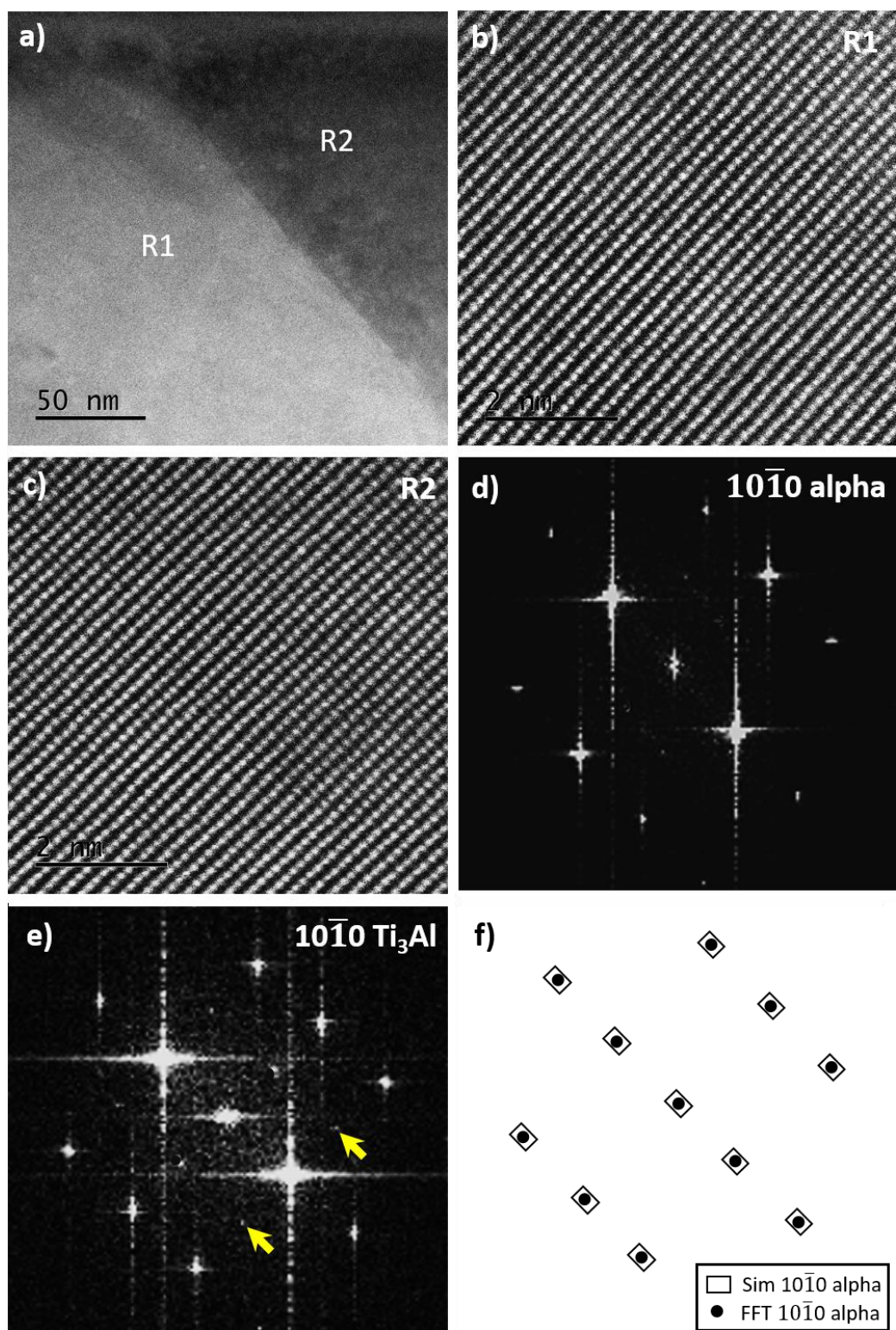


Figure 6. 14: a) HAADF STEM of hydrogen tempered martensite highlighting V rich (R1) and Al rich (R2) nanobands and atomic resolution HAADF STEM of the b) V rich and c) Al rich nanobands. Images d, e) are $[10\bar{1}0]$ zone axes fast Fourier transforms of the d) V rich and e) Al rich nanobands. Image f) confirms that V rich and Al rich nanobands have $[10\bar{1}0]$ zone axis HCP crystal structures which are at the same orientation. The additional superlattice reflections (yellow arrows in image e) confirm Ti_3Al in the f) $[10\bar{1}0]$ HCP crystal.

6.4.1.1 The nanoband interface after inadvertent hydride decomposition

Figure 6.15 a) is an atomic resolution HAADF STEM micrograph highlighting the interface (R4) of Al rich (R3) and V rich (R5) nanobands which was viewed after inadvertent hydride decomposition. **Figure 6.15** also shows the $[10\bar{1}0]$ zone axes Fourier transforms of R3, R4 and R5. The interface Fourier transform (R4) shows superimposed diffraction patterns from its surrounding nanobands. The nanoband interface is coherent after inadvertent hydride decomposition because the V rich nanoband (R5) has the same crystal structure (HCP) as the Al rich nanoband (R3). Furthermore, their HCP crystal structures are at the same crystallographic orientation.

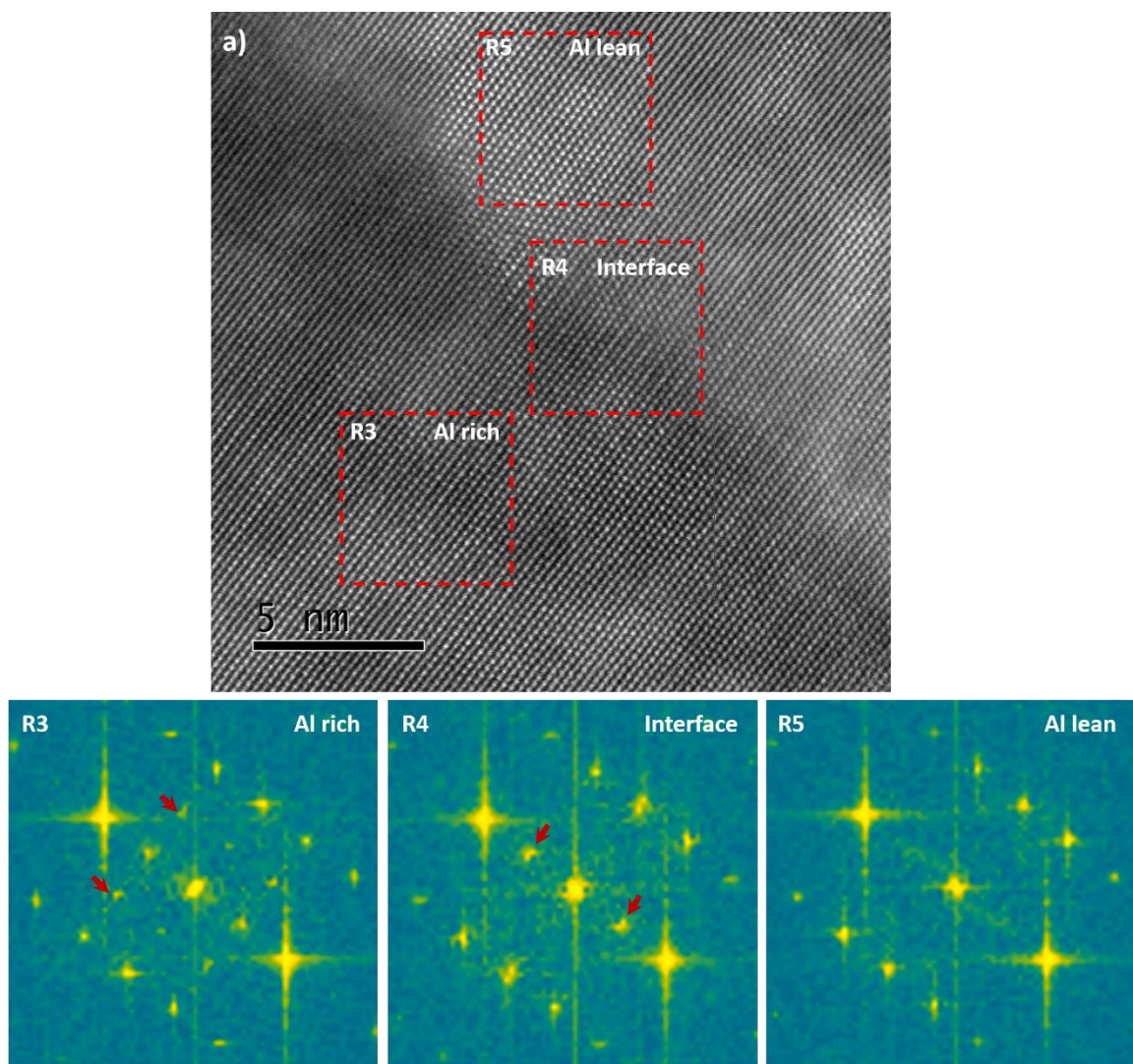


Figure 6. 15: a) Atomic resolution HAADF STEM showing the interface (R4) of Al rich (R3) and V rich (R5) nanobands and their corresponding $[10\bar{1}0]$ zone axes fast Fourier transforms. The nanoband interface has superimposed diffraction patterns from the Al rich (R3) and V rich (R5) nanobands. This is evident in the superlattice reflections (red arrows) which are diffraction contributions from the Al rich nanoband. The nanoband interface is coherent because R3 and R5 have HCP crystal structures which are at the same crystallographic orientation.

6.5 Comparing hydrogen tempered and 675°C dehydrogenated martensite to its non-hydrogen tempered and 675°C vacuum annealed counterpart

Electron transparent FIB-SEM foils were extracted from hydrogen tempered and non-hydrogen tempered martensite which was dehydrogenated or vacuum annealed at 675°C respectively. **Figures 6.16 a-c)** and **6.17 a-c)** show a) TKD phase and EDS composition maps of b) Al, c) V which compare the phase constitution and phase composition in 675°C dehydrogenated (**Figure 6.16**) or vacuum annealed (**Figure 6.17**) martensite.

The morphology of 675°C dehydrogenated martensite is acicular as shown in **Figure 6.2 g, h)**. However, its FIB-SEM section in **Figure 6.16 a)** shows a lamellar microstructure which arises from coarsened nanobands within acicular plates. **Figure 6.16 a)** also shows that the coarsened nanobands are alternate HCP and BCC phases. Comparing the latter to **Figures 6.11, 6.14** and **6.15** (which confirmed nanobands to be alternate V rich and Al rich HCP), shows that BCC phase nucleated from V rich nanobands during 675°C dehydrogenation.

The 675°C dehydrogenation differs from inadvertent hydrogen escape, because its elevated temperatures support some Al diffusion which partially dissolves Al rich nanobands and Ti_3Al . **Figure 6.16 b, c)** shows the expected partitioning of Al or V towards HCP or BCC phases. Image b) also shows a high volume fraction of retained Al rich nanobands within the HCP phase (highlighted by yellow dotted line) of 675°C dehydrogenated martensite. This means that the diffusion kinetics at 675°C do not support sufficient Al diffusion to extensively dissolve Al rich nanobands within the HCP phase. Thus 675°C dehydrogenated martensite has equilibrium composition HCP, Al rich HCP and V rich BCC phases. Comparatively, non-hydrogen tempered martensite which was vacuum annealed at 675°C (**Figure 6.17 a-c)** has equilibrium HCP and BCC phases, and an expected partitioning of Al or V towards the respective HCP or BCC phases. It has no Al rich nanobands and concomitant Ti_3Al precipitates.

Selected area diffraction (SAD) was performed at the retained Al rich nanobands of 675°C dehydrogenated martensite. **Figure 6.18** shows a, c) bright field STEM and b) HAADF STEM micrographs of 675°C dehydrogenated martensite (see **Figure 6.16**). The SAD analysis was performed at the nanobanded plate highlighted in image c). The SAD analysis in image d) confirms Ti_3Al precipitates in 675°C dehydrogenated martensite at a $[2\bar{1}\bar{1}3]$ zone axis.

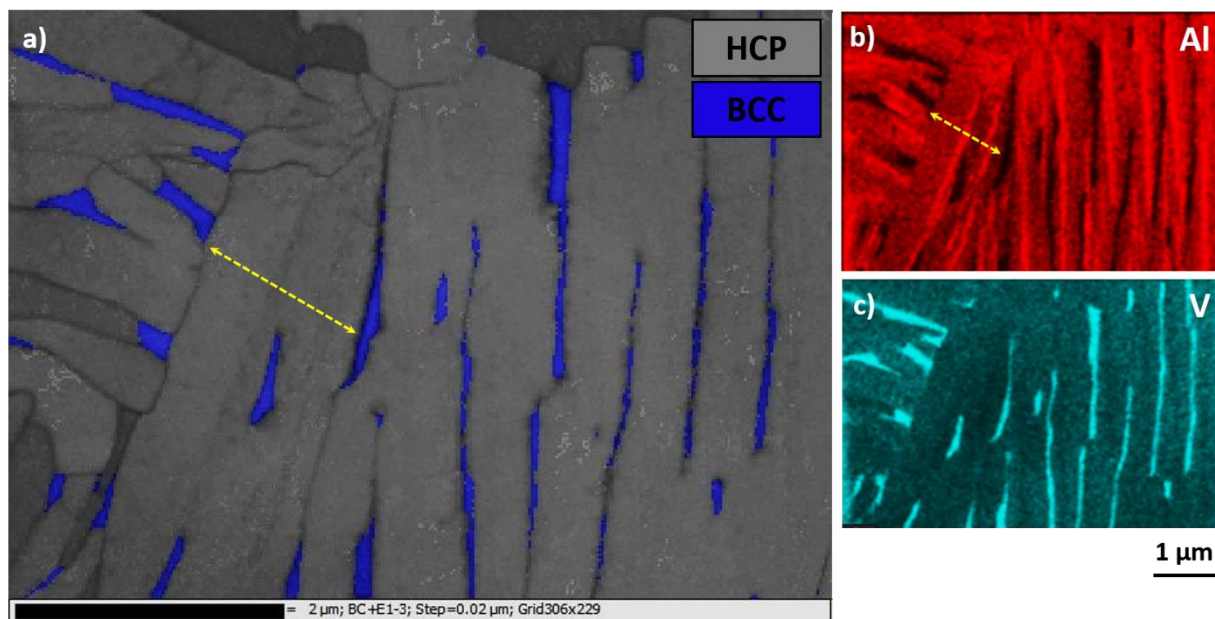


Figure 6. 16: Complementary a) TKD phase map and EDS b) Al, c) V maps of 20 at.% hydrogenated, solution treated (at 900°C), quenched, aged (at 580°C) and dehydrogenated (at 675°C) Ti-6Al-4V. Image a) shows that 675°C dehydrogenated martensite has equilibrium HCP (grey) and BCC (blue) phases. Images b) and c) show the respective partitioning of Al and V towards HCP and BCC phases. Image b) also shows retained Al rich nanobands within the HCP phase (highlighted by yellow dotted line) of 675°C dehydrogenated martensite.

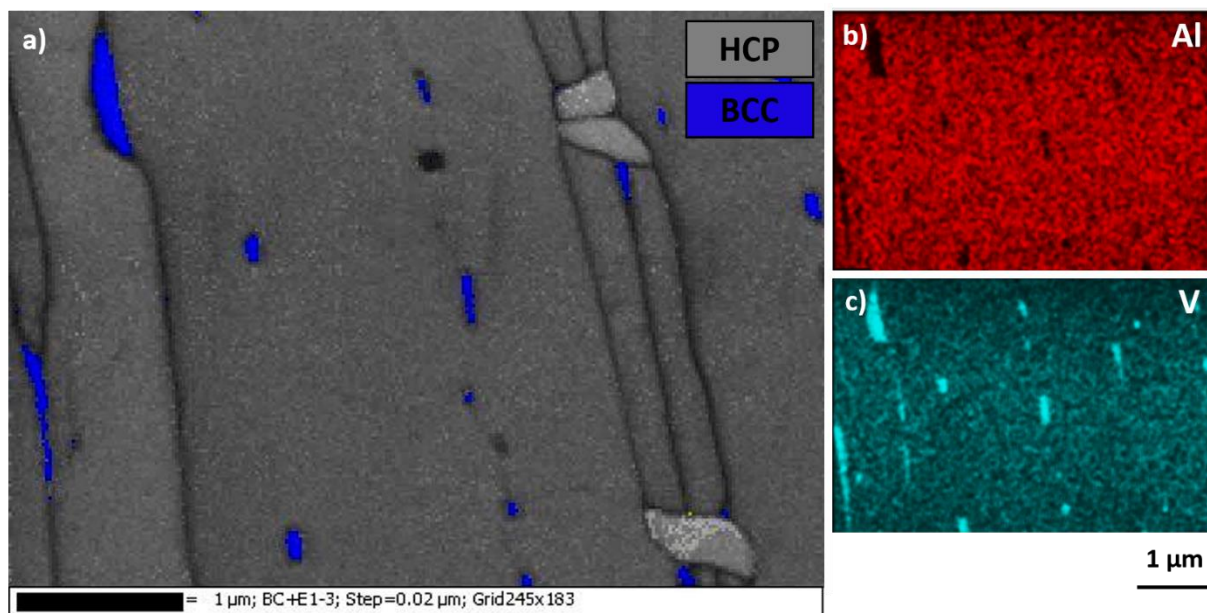


Figure 6. 17: Complementary a) TKD phase map and EDS b) Al, c) V maps of non-hydrogenated, solution treated (at 1080°C), quenched, aged (at 580°C) and vacuum annealed (at 675°C) Ti-6Al-4V. Image a) shows that 675°C vacuum annealed martensite has equilibrium HCP (grey) and BCC (blue) phases. Images b) and c) show the respective partitioning of Al and V towards HCP and BCC phases. Image b) relatively does not show any significant Al enrichment within the HCP phase of 675°C vacuum annealed martensite.

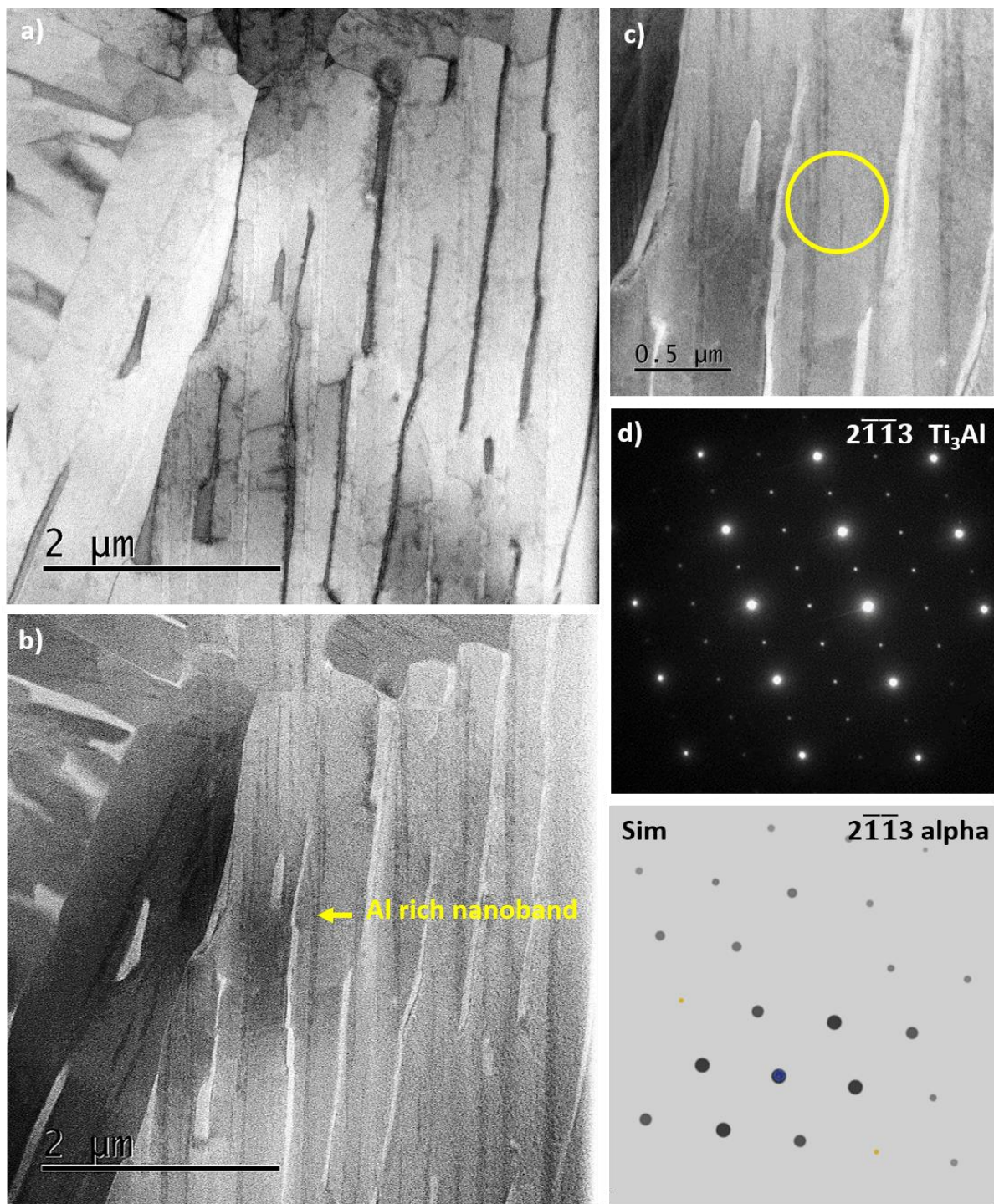


Figure 6. 18: a, c) bright field and b) HAADF STEM micrographs of 20 at.% hydrogenated, solution treated (at 900°C), quenched, aged (at 580°C) and dehydrogenated (at 675°C) Ti-6Al-4V. Selected area diffraction was performed at the highlighted region in c) and it confirmed d) Ti_3Al precipitates at a $[2\bar{1}\bar{1}3]$ zone axis. The simulated (Sim) $[2\bar{1}\bar{1}3]$ alpha pattern confirms that the attained $[2\bar{1}\bar{1}3]$ pattern is Ti_3Al not alpha. The retained Al rich nanobands in 675°C dehydrogenated martensite stabilised Ti_3Al precipitates.

6.6 Comparing hydrogen tempered and 750°C dehydrogenated martensite to its non-hydrogen tempered and 750°C vacuum annealed counterpart

Electron transparent FIB-SEM foils were extracted from hydrogen tempered and non-hydrogen tempered martensite which was dehydrogenated or vacuum annealed at 750°C respectively. **Figures 6.19 a-c)** and **6.20 a-c)** show a) TKD phase and EDS composition maps of b) Al, c) V which compare phase constitution and phase composition in the acicular plates of dehydrogenated (**Figure 6.19**) or vacuum annealed (**Figure 6.20**) martensite.

The morphology of 750°C dehydrogenated martensite is acicular as shown in **Figure 6.3 c, d)**. However, its FIB-SEM section in **Figure 6.19 a)** shows a lamellar microstructure which arises from coarsened nanobands within acicular plates. Comparing **Figures 6.16 a)** and **6.19 a)** shows that nanoband coarsening increased with dehydrogenation temperature from 675°C to 750°C. This is reiterated by comparing **Figures 6.2 h)** and **6.3 d)** and it explains the 70 MPa yield strength decrease that occurs after dehydrogenating martensite at 750°C.

Figure 6.19 a-c) shows that the coarsened nanobands are HCP and BCC phases, and that there is a respective partitioning of Al or V towards HCP or BCC phases. **Figure 6.19 b)** also shows that there are retained Al rich nanobands in 750°C dehydrogenated martensite. However, the volume fraction of retained Al rich nanobands is significantly lower in 750°C dehydrogenated martensite when compared to 675°C dehydrogenated martensite (**Figure 6.16 b)**). Comparatively, 750°C vacuum annealed martensite in **Figure 6.20 a-c)** has no retained Al rich nanobands. Instead, it has equilibrium HCP and BCC phases and an expected partitioning of Al and V towards the HCP and BCC phases respectively.

The presence of a reduced volume fraction of retained Al rich nanobands in 750°C dehydrogenated martensite indicates that the 3 hour dehydrogenation at 750°C does not fully homogenise the Al composition in hydride partitioned microstructures. The non-homogeneous Al content in 750°C dehydrogenated microstructures was observed in both HDH treated (see **Figure 5.6**) and THP treated (see **Figure 6.19**) Ti-6Al-4V. Consequently, 750°C dehydrogenated martensite was characterised in the TEM to determine if the retained Al rich nanobands stabilised Ti_3Al precipitates.

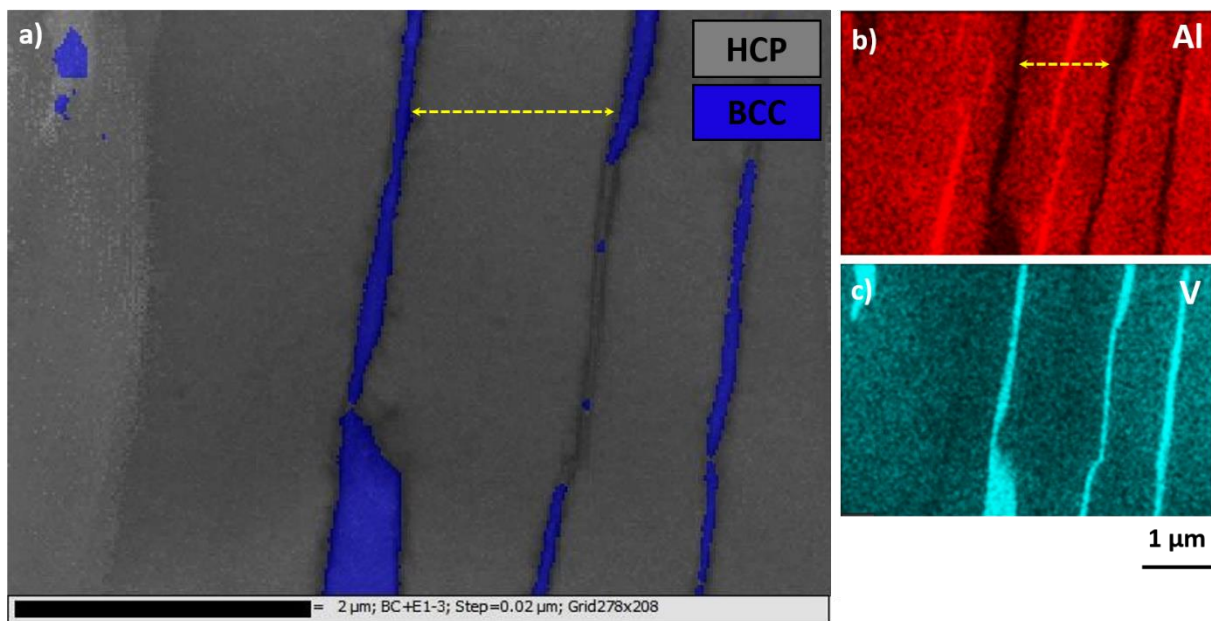


Figure 6. 19: Complementary a) TKD phase map and EDS b) Al, c) V maps of 20 at.% hydrogenated, solution treated (at 900°C), quenched, aged (at 580°C) and dehydrogenated (at 750°C) Ti-6Al-4V. Image a) shows that 750°C dehydrogenated martensite has HCP (grey) and BCC (blue) phases. Images b) and c) show the respective partitioning of Al and V towards HCP and BCC phases. Image b) also shows a decreased volume fraction of retained Al rich nanobands within the HCP phase (see yellow line) of 750°C dehydrogenated martensite.

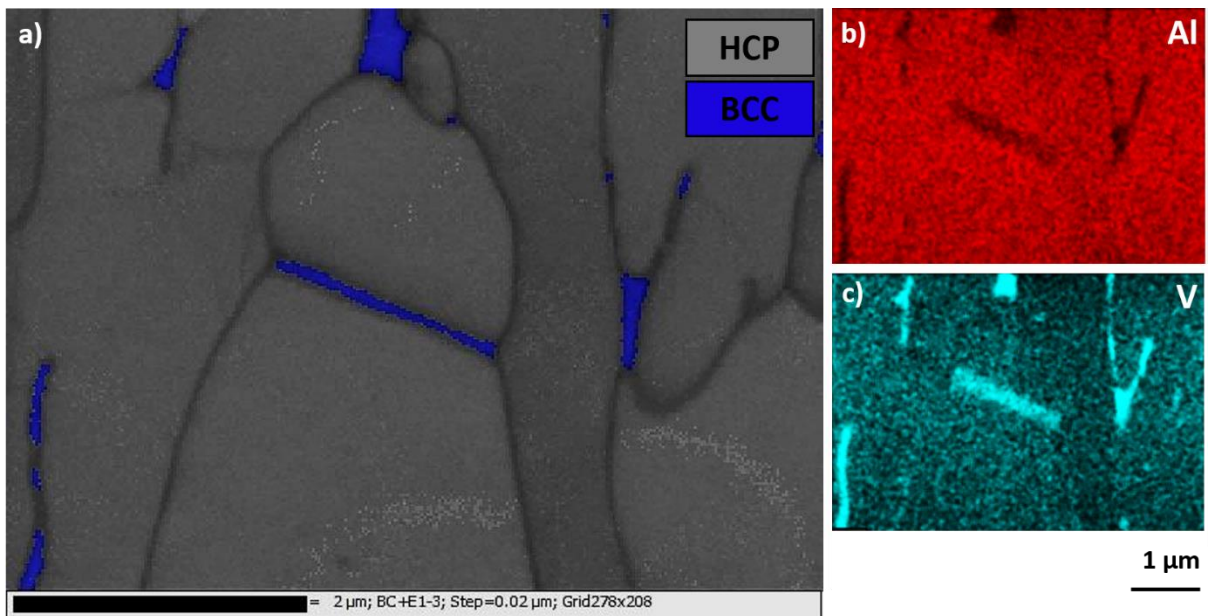


Figure 6. 20: Complementary a) TKD phase map and EDS b) Al, c) V maps of non-hydrogenated, solution treated (at 1080°C), quenched, aged (at 580°C) and vacuum annealed (at 750°C) Ti-6Al-4V. Image a) shows that 750°C vacuum annealed martensite has HCP (grey) and BCC (blue) phases. Images b) and c) show the respective partitioning of Al and V towards HCP and BCC phases. There are no retained Al rich nanobands within the HCP phase of 750°C vacuum annealed martensite.

Figure 6.21 characterises 750°C dehydrogenated martensite at atomic resolution. **Figure 6.21 a)** shows a HAADF STEM micrograph highlighting the V rich nanoband (R6) and the 750°C retained Al rich nanoband (R7). **Figure 6.21 b, c)** shows atomic resolution HAADF STEM micrographs which reveal the arrangement of atomic columns in the b) V rich nanoband and c) Al rich nanoband. **Figure 6.21 d, e)** shows reduced fast Fourier transforms which reveal the crystal structure of the d) V rich and e) the Al rich nanobands. The simulated (Sim) pattern in **Figure 6.21** is a $[2\bar{1}\bar{1}6]$ zone axis alpha diffraction pattern.

Figure 6.19 a-c) showed that 750°C dehydrogenated martensite has V rich BCC, equilibrium composition HCP and 750°C retained Al rich nanobands. The latter is also observed in **Figure 6.21 a)**, where V rich or Al rich nanobands are respectively highlighted by the bright or dark atomic Z-contrast. Comparing the arrangement of atomic columns in **Figure 6.21 b, c)** reveals that the b) V rich and c) Al rich nanobands in 750°C dehydrogenated martensite have different crystal structures. This is contrary to what was observed in hydrogen tempered martensite (in **Figure 6.14 b, c)** where the V rich and Al rich nanobands had the same HCP crystal structure. This shows that 750°C dehydrogenation supports the nucleation of BCC phase from decomposing V rich hydrides.

The nucleation of BCC phase from decomposing V rich hydrides is also confirmed by the Fourier transforms of V rich and Al rich nanobands in **Figure 6.21 d, e)**. The fast Fourier transform of the V rich nanoband (R6) confirms BCC phase at a $[102]$ zone axis. Comparing this to **Figures 6.11, 6.14** and **6.15** (which confirmed nanobands as alternate V rich, Al rich HCP phase), shows that BCC phase nucleated from V rich nanobands during 750°C dehydrogenation.

The fast Fourier transform of the Al rich nanoband (R7) confirms Ti_3Al at a $[2\bar{1}\bar{1}6]$ zone axis. The presence of superlattice reflections in the $[2\bar{1}\bar{1}6]$ Fourier transform (which are absent in the simulated $[2\bar{1}\bar{1}6]$ HCP pattern) unambiguously confirms Ti_3Al precipitates in 750°C dehydrogenated martensite. Notwithstanding this, HDH treatment showed that 750°C dehydrogenation supports extensive Al diffusion which significantly dissolves Al rich clusters to extents that almost restore full ductility. Thus the volume fraction of Ti_3Al that is present in 750°C dehydrogenated microstructures has an insignificant effect on ductility.

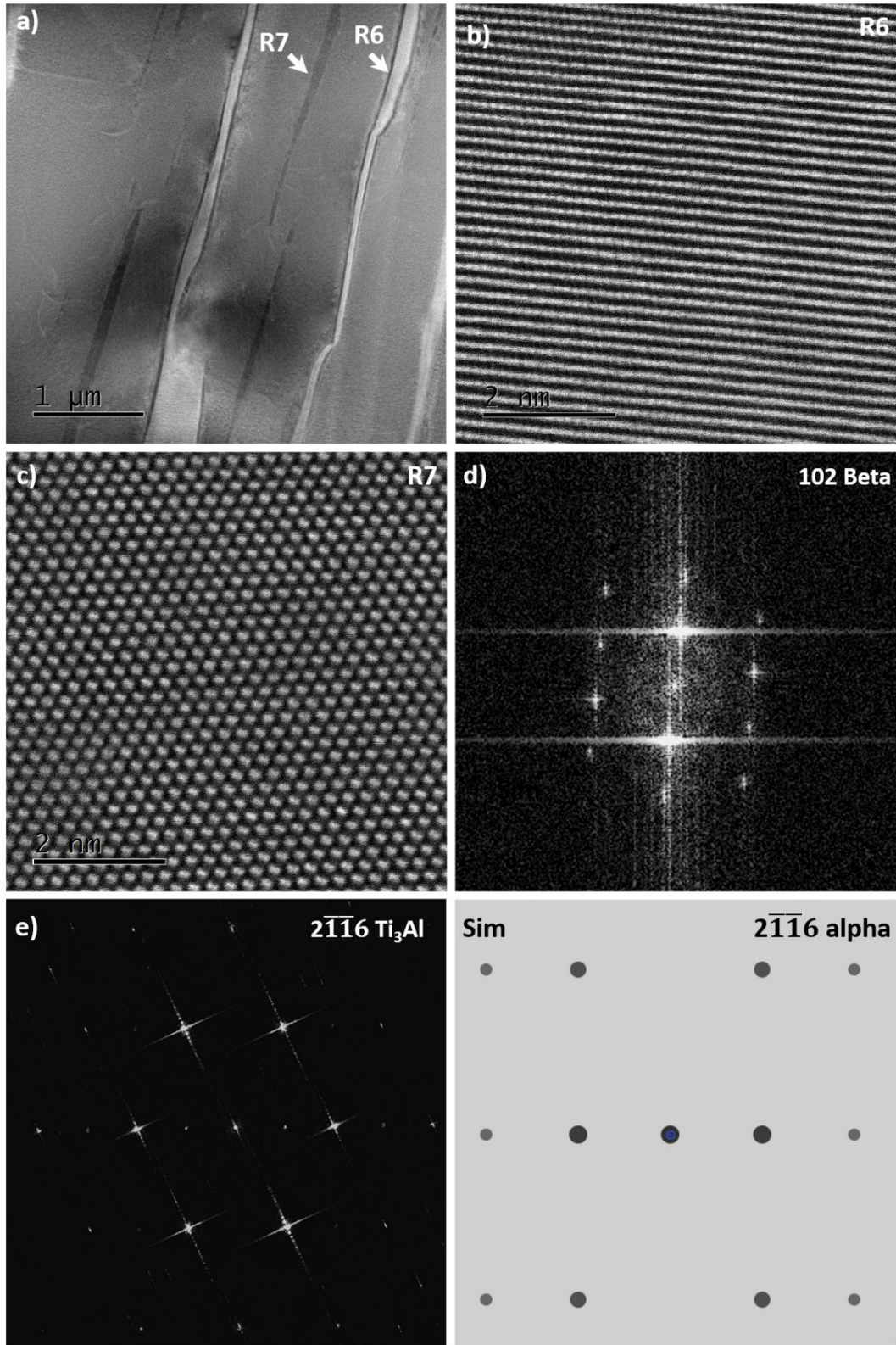


Figure 6. 21: a) HAADF STEM of 750°C dehydrogenated martensite highlighting V rich (R6) and Al rich (R7) nanobands and atomic resolution HAADF STEM obtained from the b) V rich and c) Al rich nanobands. Images d, e) are fast Fourier transforms of the d) V rich and e) Al rich nanobands. The Fourier transforms confirm d) BCC phase at a [102] zone axis and e) Ti₃Al precipitates at a $[2\bar{1}\bar{1}\bar{6}]$ zone axis. The simulated $[2\bar{1}\bar{1}\bar{6}]$ alpha diffraction pattern is significantly different, confirming that the $[2\bar{1}\bar{1}\bar{6}]$ Fourier transform in e) is Ti₃Al not alpha.

6.7 Elements of hydrogenation-disproportionation in hydrogen tempered martensite

Hydrogenated, solution treated and quenched martensite has a hydrogen stabilised metastable BCC phase and HCP martensite plates. Therefore elements of hydrogenation-disproportionation were assessed from the evolution of metastable BCC phase and HCP martensite plates during hydrogen tempering.

6.7.1 Microstructure evolution during hydrogen tempering

Martensite plates

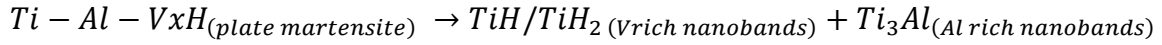
- Hydrogen tempering nucleates V rich nanobanded hydrides within tempered martensite plates.
- The nanobanded hydrides subsequently partition Al to neighbouring nanobands where the consequent Al enrichment stabilises Ti_3Al .

Metastable beta

- During hydrogen tempering, metastable beta transforms to HCP alpha, and Al diffuses towards the present volume fraction of HCP phase (including tempered plate martensite and the nucleated HCP alpha phase).
- The nucleated alpha is saturated with hydrogen and this promotes hydride precipitation in the interplate region.
- Linear hydride precipitates nucleate at the boundaries of HCP variants (this could be tempered plate martensite or the nucleated alpha phase) and are therefore adjacent to the HCP phase.
- **Chapter 6** demonstrates the partitioning of Al from nanobanded hydrides at atomic resolution. It can thus be inferred that linear hydrides similarly partitioned Al to neighbouring HCP regions where the consequent Al enrichment stabilised Ti_3Al . This inferred role is validated in **Chapter 7**.

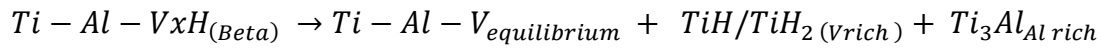
6.7.2 Elements of a hydrogenation-disproportionation reaction

A disproportionation reaction is a chemical reaction where a molecule transforms into two or more dissimilar products that are different chemical species.⁷¹ Hydrogen tempering transformed martensite plates into distinct Al rich and V nanobands which ultimately stabilised Ti₃Al precipitates and beta grains. Therefore the hydrogenation-disproportionation half reaction for hydrogen tempered martensite plates can be described by **Equation 10**;



Equation 10

Hydrogen tempering also transformed metastable beta into equilibrium composition HCP phase, Al rich HCP phase, and V rich regions. The latter ultimately stabilised equilibrium alpha, Ti₃Al precipitates and refined beta phase respectively. The hydrogenation-disproportionation half reaction for hydrogen tempered metastable beta can be described by **Equation 11**;



Equation 11

Hydrogen tempered martensite shows some microstructure evolution elements that are proposed to occur during hydrogenation-disproportionation. However, it does not reflect all of the proposed elements:

- *The proposed elements that show in hydrogen tempered martensite*
Nanobanded hydride precipitates are lean in aluminium and they have neighbouring Al enriched nanobands where the degree of Al enrichment stabilises Ti₃Al precipitates.
- *The proposed elements that do not show in hydrogen tempered martensite*
Nanobanded hydrides are rich in vanadium, this indicates that vanadium was not rejected from hydrides as proposed in literature (see **Section 2.6.2.1**).

Section 6.7 supports the hypothesis which states that hydrogenation-disproportionation accounts for the evolution of grain refinement and the promotion of Ti₃Al formation in hydrogen treated Ti-6Al-4V. However, there is an unexpected but observed enrichment of nanobanded hydrides with vanadium. This reveals that beta grains nucleate from decomposing hydrides, and not V rich regions that formed as a consequence of hydrides rejecting vanadium.

6.8 Summary of the contribution of hydrogen to the evolution and the tensile performance of tempered martensite

6.8.1 Tensile performance after 675°C dehydrogenation or vacuum annealing

The THP 900-580-675 treatment increases simulated cast Ti-6Al-4V strength by 130 MPa (YS) and 142 MPa (UTS) but it decreases tensile ductility by 60%. The contribution of hydrogen to the observed strength increase and ductility loss was evaluated by comparing the THP 900-580-675 treatment to its non-hydrogenated counterpart. Heat treating non-hydrogenated Ti-6Al-4V under similar conditions (control 900-580-675) increases the strength by 90 MPa (YS) and 88 MPa (UTS) and decreases tensile ductility by 30%.

Therefore alloyed hydrogen contributes 40 MPa (YS), 54 MPa (UTS) to the strength increase and 30% to the ductility loss in 675°C dehydrogenated martensite. The contribution of hydrogen emanates from hydrogen promoted microstructure evolution. The latter promotes acicular plate martensite transformation at 900°C and Ti_3Al precipitation. The combined effect of the acicular morphology and Ti_3Al causes a 30% ductility loss in hydrogen tempered, 675°C dehydrogenated martensite. Although hydrogen promoted microstructure evolution plays a role in the tensile performance of tempered martensite, this performance is largely dominated by martensite formation and subsequent tempering. Therefore, hydrogen promoted microstructure evolution contributes to the tensile performance that is dominated by martensite formation and tempering.

6.8.2 Tensile performance after 750°C dehydrogenation or vacuum annealing

Increasing the vacuum annealing temperature from 675°C to 750°C decreases the non-hydrogen tempered martensite strength by 70 MPa (YS), 35 MPa (UTS) and restores 12% ductility. Similarly, increasing the dehydrogenation temperature from 675°C to 750°C decreases the hydrogen tempered martensite strength by 70 MPa (YS), 32 MPa (UTS) and restores 32% ductility. Increasing the vacuum annealing or dehydrogenation temperature from 675°C to 750°C coarsens acicular plates and softens martensite. The extent of 750°C martensite softening is similar in hydrogen tempered and non-hydrogen tempered martensite. Offsetting the 12% recovered ductility that is owed to martensite softening leaves a net 20% ductility which is caused by Ti_3Al dissolution at 750°C.

6.8.3 Hydrogen tempered and non-hydrogen tempered martensite

Hydrogenated martensite has a hydrogen stabilised metastable BCC phase. The beta stabilising effect of hydrogen prevents a full BCC to HCP plate martensite transformation during quenching. Comparatively, non-hydrogenated martensite does not have a metastable BCC phase. It undergoes a full BCC to HCP transformation during quenching.

Tempering at 580°C for 3 hours precipitates Ti_3Al in hydrogenated martensite but it does not precipitate Ti_3Al in non-hydrogenated martensite. This is because hydrogen tempering decomposes the metastable BCC phase to HCP phase. The BCC to HCP transformation saturates the HCP phase with hydrogen; this ultimately precipitates fine hydrides, or linear hydrides in the interplate region and nanobanded hydrides within martensite plates. Hydride precipitates partition Al. The Al that is partitioned from hydride nanobands enriches neighbouring nanobands to critical concentrations that stabilise Ti_3Al . The extensive Al enrichment is not observed in non-hydrogen tempered martensite because it has no hydrides.

6.8.3.1 Nanobanded hydrides in hydrogen tempered martensite

The nanobanded morphology is a typical hydride morphology that occurs when hydrides configure to a particular nucleation interface. In this study, the nanobanded morphology was observed within tempered martensite plates. Vanadium rich hydrides partition Al, this enriches neighbouring nanobands with Al and causes the periodic variation in Al and V composition that is characteristic to the nanobanded morphology. The nanobanded morphology is not observed in non-hydrogen tempered martensite because the latter has no hydride precipitates.

The nanobanded morphology is observed as alternate V rich and Al rich alpha in electron transparent samples. This is because inadvertent hydrogen escape decomposes hydride precipitates to V rich alpha. However, this room temperature hydride decomposition does not affect the extensive Al enrichment that is caused by hydride induced partitioning in neighbouring Al rich nanobands. Therefore, the nanobanded morphology is seen as alternate V rich alpha and Ti_3Al nanobands in electron transparent samples. The nanoband interface is coherent after inadvertent hydride decomposition because Al rich and V rich nanobands retain HCP crystal structures that are at the same crystallographic orientation.

6.8.4 Tempered microstructure recombination after 675°C dehydrogenation

The tempered and 675°C dehydrogenated microstructure is partially recombined. It has a high volume fraction of retained Al rich nanobands which stabilise Ti_3Al precipitates. This explains why 675°C dehydrogenated martensite has a 30% ductility loss which is partially caused by Ti_3Al precipitates. Dehydrogenating martensite at 675°C nucleates equilibrium BCC phase at V rich nanobands to form a partially recombined microstructure. The partially recombined microstructure consists of equilibrium composition HCP alpha, a high volume fraction of retained Al rich nanobands within HCP phase (which stabilises a significant volume fraction of Ti_3Al) and some V rich BCC phase.

6.8.5 Tempered microstructure recombination after 750°C dehydrogenation

The 750°C dehydrogenated martensite has relatively coarse nanobands compared to 675°C dehydrogenated martensite. The martensitic microstructure significantly coarsens after dehydrogenating at 750°C. This causes a 70 MPa (YS) and approximately 30 (UTS) strength loss.

The tempered and 750°C dehydrogenated microstructure is significantly recombined. It has a significantly reduced volume fraction of retained Al rich nanobands. Dehydrogenating martensite for 3 hours at 750°C does not fully homogenise the microstructure. It retains some Al rich nanobands which also stabilise Ti_3Al .

The non-homogeneous Al content in 750°C dehydrogenated microstructures was also observed in HDH treated Ti-6Al-4V. Notwithstanding the latter, HDH treatment showed that 750°C dehydrogenation supports extensive Al diffusion which significantly dissolves Al rich clusters to extents that almost restore full ductility. Thus the volume fraction of Ti_3Al that may be present in 750°C dehydrogenated microstructures has an insignificant effect on ductility. This explains why dehydrogenating martensite at 750°C recovers 30% ductility. Since martensite softening recovers 10% ductility, the net 20% recovered ductility is caused by Ti_3Al dissolution at 750°C. In conclusion, 750°C dehydrogenated martensite has retained Ti_3Al but its volume fraction has an insignificant influence on the ductility.

CHAPTER 7: THERMOHYDROGEN AND DEFORMATION PROCESSING

Chapter 6 compared hydrogen tempered and non-hydrogen tempered martensite to highlight the influence of hydrogen tempering on martensite evolution. Hydrogen tempering promoted the nanobanded morphology and Ti_3Al precipitation at short aging times (3 hours).

Chapter 7 elaborates on the evolution of the nanobanded morphology and articulates the contribution of hydrogen to the latter. It also demonstrates the effect of hydride precipitates on the enrichment of adjacent HCP regions with Al and concomitant Ti_3Al precipitates.

Chapter 7 highlights grain and morphology evolution during the transient stages of the THDP treatment. It emphasises the degree of grain and morphology refinement that can be achieved from THDP processing.

As-cast Ti-6Al-4V was hydrogenated (to 20 at.%H), hot deformed (true strain 1.6 at 10s^{-1} rate), recrystallized (at 900°C for 15 minutes) plus quenched, aged (at 580°C for 3 hours) and dehydrogenated (at 675°C for 3 hours). Samples were extracted at the quenched, aged and 675°C dehydrogenated stages to trace microstructure evolution during THDP treatment.

Chapter 7 concludes that the nanobanded morphology is caused by nucleation of hydrides at nanosized shear bands within martensite plates. The nanosized shear bands are a lattice invariant deformation that occurs within martensite plates to accommodate Bain strain. It also concludes that self-accommodation governs the nucleation of HCP variants during martensite transformation and subsequent tempering. Self-accommodation groups HCP variants to self-repeating patterns that limit the strain induced on the non-transformed BCC region. Consequently, selected HCP variants (out of the expected 12) nucleate at the quenched, aged and dehydrogenated stages of the THDP treatment. The selected variants are configured to a 2 or 3 variant cluster morphologies known as indentation mark or triangular morphologies. Linear or nanobanded hydrides partition Al and this extensively enriches adjacent HCP plates or nanobands with Al to critical levels that stabilise Ti_3Al . The extensively enriched regions, and Ti_3Al precipitates are retained after dehydrogenating at 675°C .

7.1 The recrystallised and quenched THDP microstructure

Figure 7.1 shows an EBSD phase map of the recrystallised and quenched THDP microstructure. To produce the latter, as-cast Ti-6Al-4V was hydrogenated (to 20 at.%H), hot deformed (true strain 1.6 at 10s^{-1} rate), recrystallized (at 900°C for 15 minutes) and quenched.

In **Figure 7.1**, the recrystallized and quenched THDP microstructure has HCP acicular martensite plates and BCC interplate regions. Recrystallisation refined the prior beta grain size diameter from $2000\text{ }\mu\text{m}$ to approximately $10\text{-}20\text{ }\mu\text{m}$. Alloyed hydrogen prevented a full BCC to HCP martensite transformation and stabilised some of the high temperature BCC phase as a metastable phase at room temperature.

7.1.1 Martensite transformation

Quenching from 900°C caused a diffusionless BCC to HCP martensite plate transformation. The martensite plate transformation occurs in a series of transformation events, this results in successive generations of martensite plates which get progressively smaller in size.¹¹⁰ Undercooling promotes nucleation of first generation martensite plates. This transformation progresses by moving the martensite plate interface into the parent BCC grain until interface coherency is lost.¹¹⁰ The martensite transformation strain is accommodated by lattice invariant deformation (twinning or slip within martensite plates) or plastic deformation of the parent BCC grain. The dislocations exerted by previous generations of martensite plates on the BCC parent are nucleation points for successive generations.¹¹⁰ However the dislocations also limit the growth of successive generations, and thus they progressively get smaller in size.

7.1.2 Strain accommodation during martensite transformation

The phenomenological theory of martensite crystallography (PTMC)¹¹⁰⁻¹¹² states that a martensite transformation retains an undistorted and unrotated invariant plane (habit plane) between the parent and the product. This requires a crystal structure deformation (to transform the BCC crystal to HCP martensite crystal), a lattice invariant deformation in the form of slip or twinning (to orient the geometric shape of the martensite crystal in a manner that creates an invariant plane) and a rigid body rotation (to ensure the invariant plane remains unrotated).

The Bain strain transforms the parent crystal structure (BCC) to martensite's crystal structure (HCP), but it is an invariant line deformation which has high strain energy. This strain energy is accommodated by lattice invariant deformation and plastic deformation of the BCC parent. The Bain strain requires a lattice invariant deformation which changes the geometric shape of martensite to create an invariant plane (without altering its HCP crystal structure). Lattice invariant deformation is achieved by adding the necessary magnitude of slip or twinning within martensite plates to create an invariant plane. The invariant plane maintains a coherent interface between the propagating martensite plate and the non-transformed BCC parent. The martensite plate stops propagating into the parent BCC grain after losing interface coherency.

Lattice invariant deformation is commonly observed as twinning of orthorhombic martensite plates in hydrogenated Ti-6Al-4V literature.^{16, 50} However, in this study lattice invariant deformation was observed as slip bands occurring within hexagonal martensite plates. **Figure 7.2** is atomic resolution HAADF STEM micrograph showing the substructure of a HCP martensite plate in the quenched THDP sample. The atomic columns within the martensite plates are nanobanded because of nanosized, linear crystal defects or slip bands. The nanosized slip bands are caused by lattice invariant deformation which occurs during martensite transformation.

7.1.3 Variant selection of martensite plates

Martensite plates self-accommodated¹¹³ into groups or patterns to minimise the strain energy that is exerted on the non-transformed BCC parent. Self-accommodation couples the strain energy exerted by martensite plates to a small region. This reduces the strain energy that could otherwise be induced by ungrouped plates on the BCC parent.

Figure 7.3 is an Euler colour map of the recrystallized and quenched THDP sample. **Figure 7.3** shows that selected HCP plate variants nucleated during the BCC to HCP martensite transformation. The selected variants grouped into self-repeating patterns of 2 or 3 variant clusters to form triangular (1) or indentation mark (2) morphologies.¹¹³

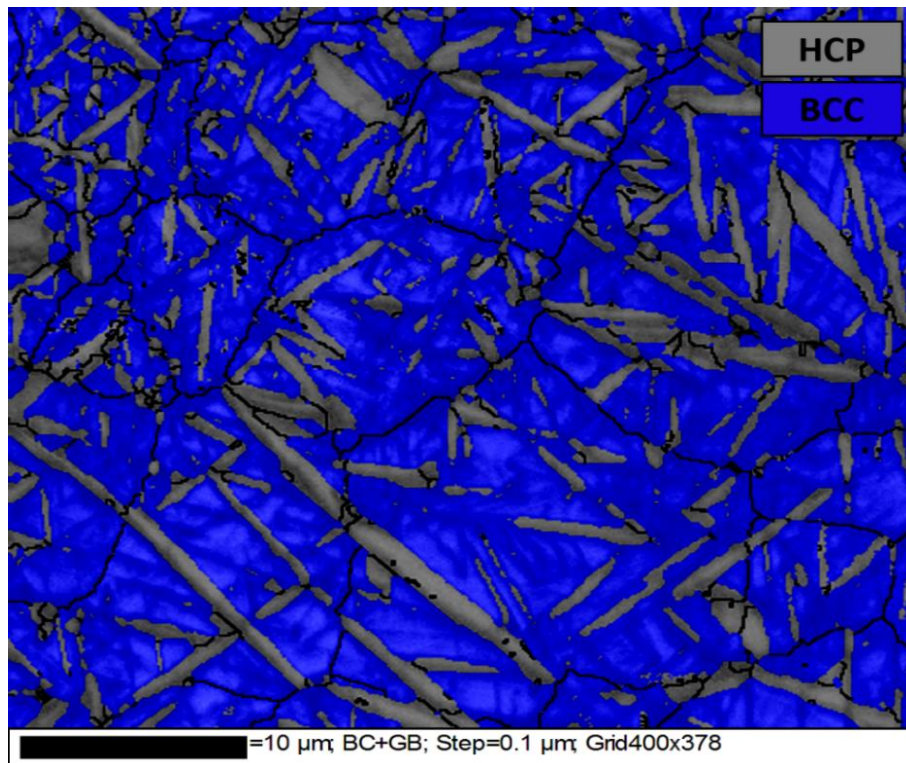


Figure 7. 1: EBSD phase map of a recrystallised and quenched THDP microstructure showing HCP martensite plates (grey) and a hydrogen stabilised BCC interplate region (blue). The black lines demarcate grain boundaries with a misorientation angle greater than 15° .

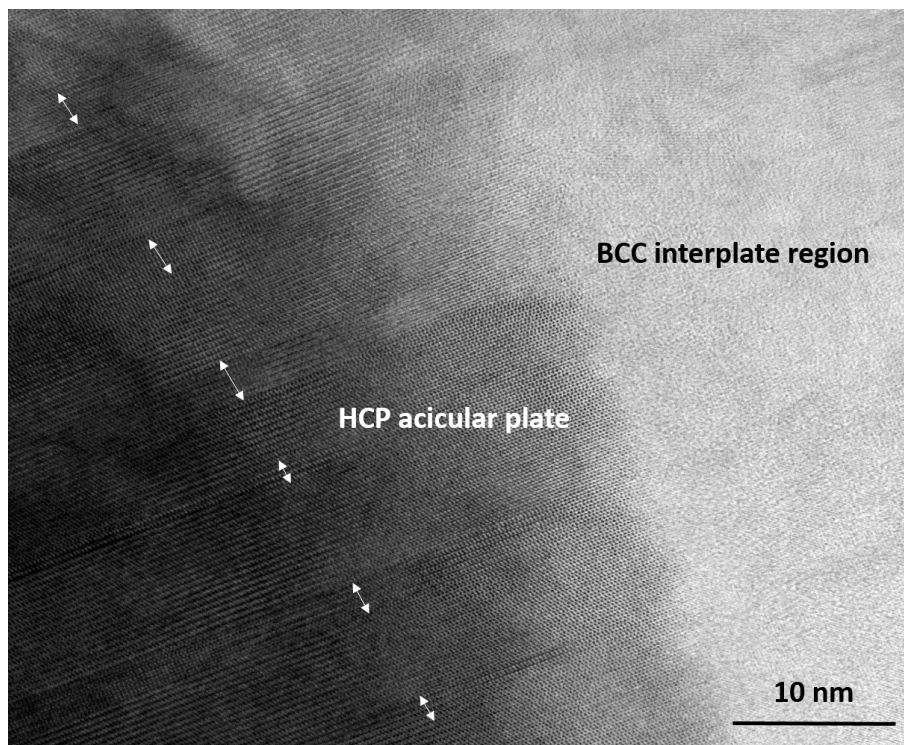


Figure 7. 2: Atomic resolution HAADF STEM highlighting (white arrows) evidence of lattice invariant deformation within the HCP martensite plates of the quenched THDP microstructure. The lattice invariant deformation is observed as nanosized, linear crystal defects or slip bands which form nanobanded atomic columns within martensite plates.

The Burgers relationship determines 12 possible HCP plate variants that can nucleate during a BCC to HCP transformation. **Figure 7.3**, shows that a few HCP plate variants nucleated during the BCC to HCP martensite transformation out of the expected 12. This is because increasing the degree of self-accommodation promotes variant selection whereby specific martensite plate variants are selected because they offer optimum groupings which induce the lowest strain energy.

The drive to achieve the highest degree of self-accommodation and concomitant reduction in strain results in nucleation of selected HCP plate variants which offer optimum groupings.¹¹⁴ This leads to the nucleation of a selected few HCP martensite variants which form self-repeating patterns of preferred groupings in successive plate generations. **Figure 7.3** shows the self-repeating patterns as 2 or 3 HCP variant cluster morphologies that are configured to indentation mark (2)¹¹³ or triangular morphologies (1).¹¹³

Figure 7.4 shows a bright field TEM micrograph and complementary SAD patterns attained at regions R1 and R2, where R1 is the acicular plate (R1) and R2 is the interplate region (R2) of the recrystallised and quenched THDP microstructure. The complementary R1 and R2 SAD patterns confirm HCP martensite and BCC beta phases at zone axes $[10\bar{1}1]$ and $[001]$ respectively. The absence of superlattice reflections in the simulated $[10\bar{1}1]$ Ti_3Al SAD pattern confirms that the attained $[10\bar{1}1]$ zone axis pattern is alpha not Ti_3Al . Nevertheless, Ti_3Al precipitates are not expected because the THDP microstructure was quenched from a fully beta region. Therefore SAD reiterates that the quenched THDP microstructure has HCP martensite plates and a hydrogen stabilised BCC interplate region.

Figure 7.5 a-c) shows the elemental composition of the recrystallised and quenched THDP microstructure at the HCP plate and BCC interplate regions. The EDS maps (**Figure 7.5 b, c**) show no significant variation in aluminium (Al) or vanadium (V) content at the HCP plate and BCC interplate regions. This is confirmed by EDS point analysis (**Figure 7.5 d**) which quantifies an average of 11at.%Al and 4at.%V at points 1-6 which span across the HCP plate and BCC interplate region. The uniform composition confirms that the microstructure was quenched from a fully BCC region and that the BCC to HCP martensite plate transformation was diffusionless. The latter enabled the martensite plates to retain the parent BCC composition.

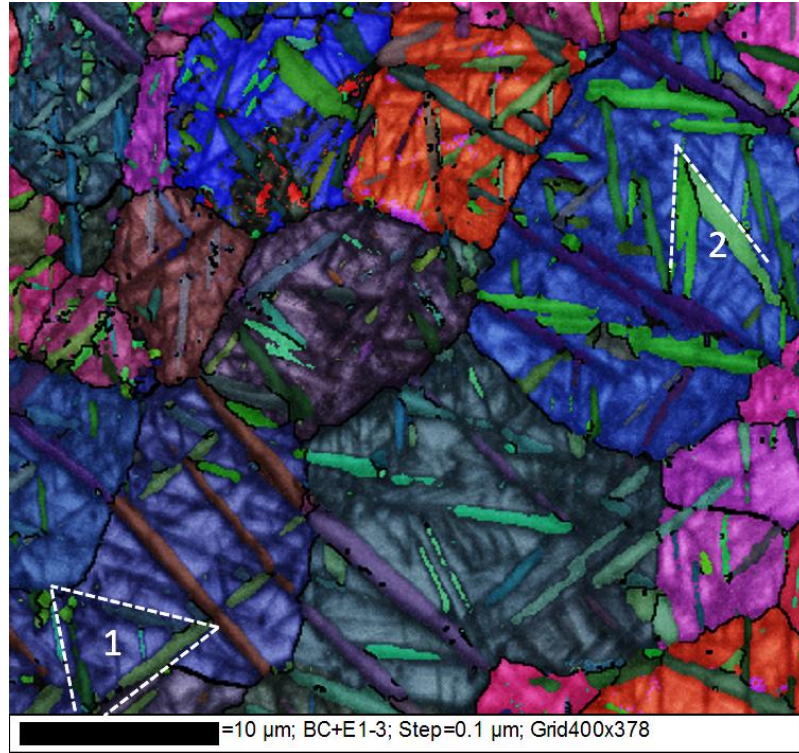


Figure 7. 3: a) Euler colour map of the recrystallised and quenched THDP microstructure showing variant selected and self-accommodated HCP plates which are configured to triangular (1) or indentation mark (2) morphologies. Black lines demarcate grains with a misorientation angle above 15° .

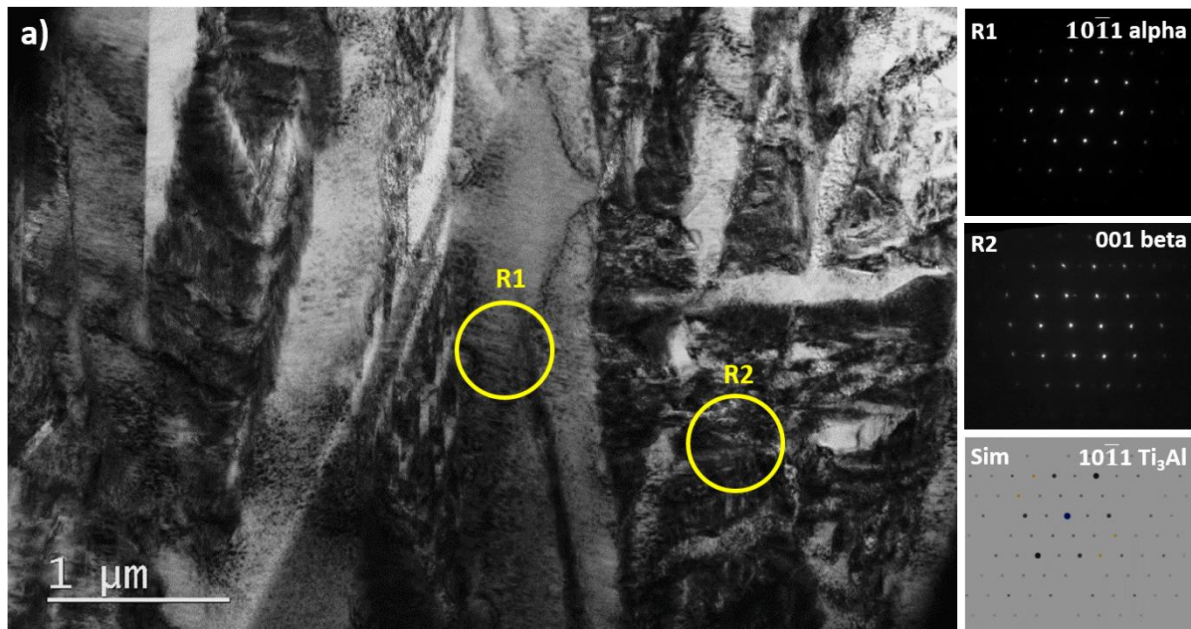


Figure 7. 4: Bright field TEM highlighting (R1) martensite plate and (R2) interplate regions. The corresponding SAD patterns confirm $[10\bar{1}1]$ HCP martensite and $[001]$ beta at regions R1 and R2 respectively. The simulated $[10\bar{1}1]$ Ti_3Al SAD pattern validates that the attained HCP $[10\bar{1}1]$ zone axis pattern is HCP martensite and not Ti_3Al phase.

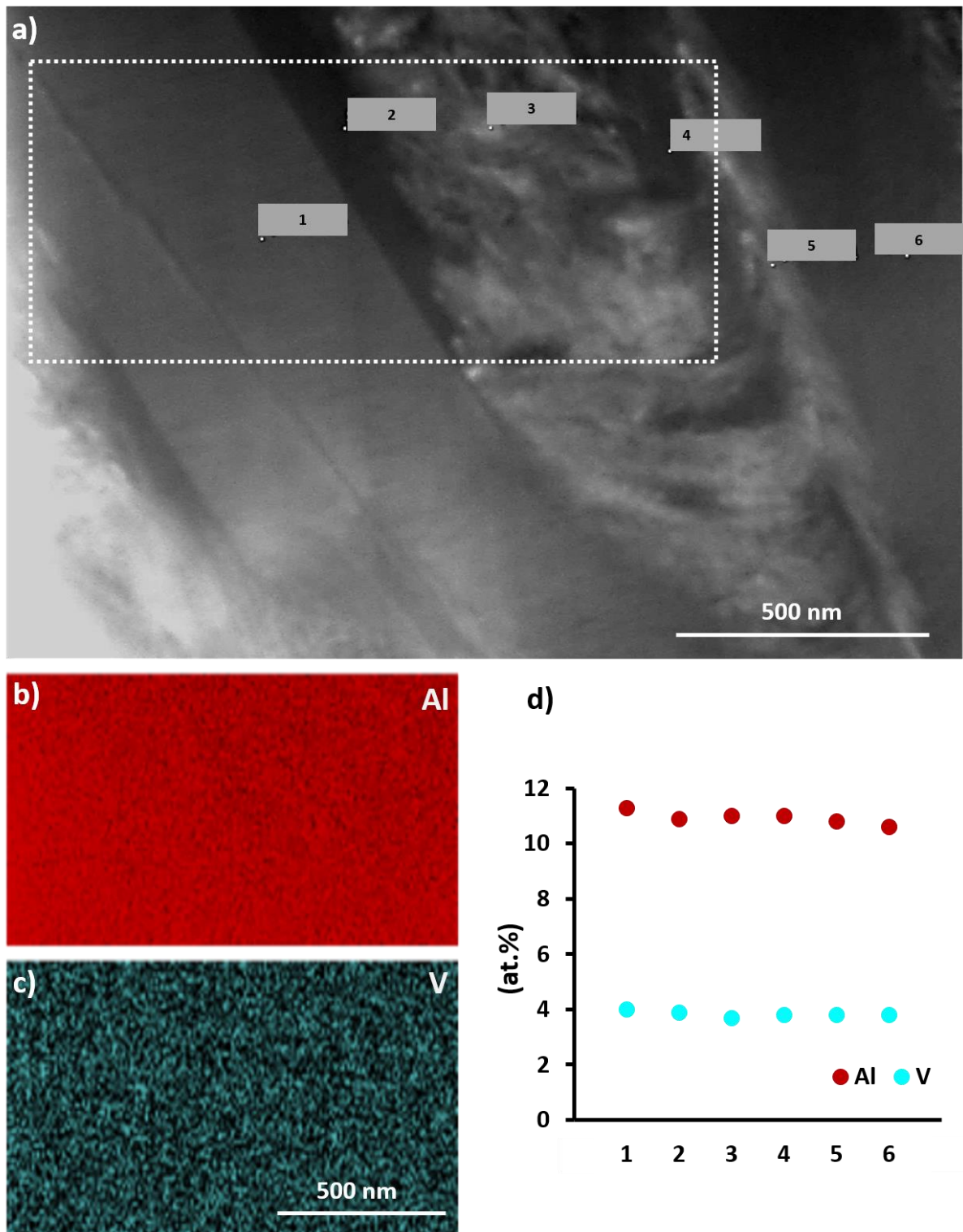


Figure 7. 5: a) HAADF STEM highlighting martensite plate and interplate regions. Complementary EDS b) aluminium (Al) and c) vanadium (V) maps and d) EDS point analyses (1-6) were performed at the highlighted regions which span across acicular plate and interplate regions. The EDS maps in b, c) show no significant difference in Al, V content between the martensite plate and interplate regions. This is confirmed by EDS point analysis in d) which shows an average Al and V concentration of $11 \pm 0.2 \text{ at.\%Al}$ and $4 \pm 0.2 \text{ at.\%V}$ respectively at points 1-6.

7.2 Phase constitution in the aged THDP microstructure

Figure 7.6 a, b) shows EBSD phase and Euler colour maps of the 580°C aged THDP microstructure. To produce the latter, as-cast Ti-6Al-4V was hydrogenated (to 20 at.%H), hot deformed (true strain 1.6 at 10s⁻¹ rate), recrystallized (at 900°C for 15 minutes) plus quenched and aged (at 580°C for 3 hours).

Figure 7.6 a) shows that the aged THDP microstructure has HCP alpha and FCC, FCT hydrides. Aging decomposed metastable beta (BCC) to nucleate refined HCP alpha and hydrides. **Figure 7.6 b)** shows that the nucleated alpha variants retained the orientation and morphological configuration (indentation mark or triangular) that is observed in the tempered martensite plates. This indicates that aging nucleated selected alpha variants that retained the self-accommodated groupings of tempered martensite plates.¹¹⁴

The aged THDP microstructure has fine hydride, linear hydride and nanobanded hydride precipitates. Linear hydrides nucleated in the interplate region adjacent to martensite plate boundaries (see red arrow in **Figure 7.6 a)**). Martensite plate boundaries are high energy points which provided linear nucleation interfaces that configured nucleating hydrides to a linear hydride morphology.

Nanobanded hydrides nucleated within tempered martensite plates (orange arrow in **Figure 7.6 a)**). Nanobanded hydrides maintained the orientation of the parent tempered martensite plate because there is no change in orientation that is observed within tempered martensite plates in **Figure 7.6 b)**. This indicates a coherent epitaxial growth¹¹⁵ of nanobanded hydrides within tempered martensite plates. Lattice invariant deformation induced nanosized slip bands in the substructure of quenched martensite plates (see **Figure 7.2)**. The nanosized slip bands are high energy points which provided nanobanded nucleation interfaces that configured nucleating hydrides to a nanobanded morphology.

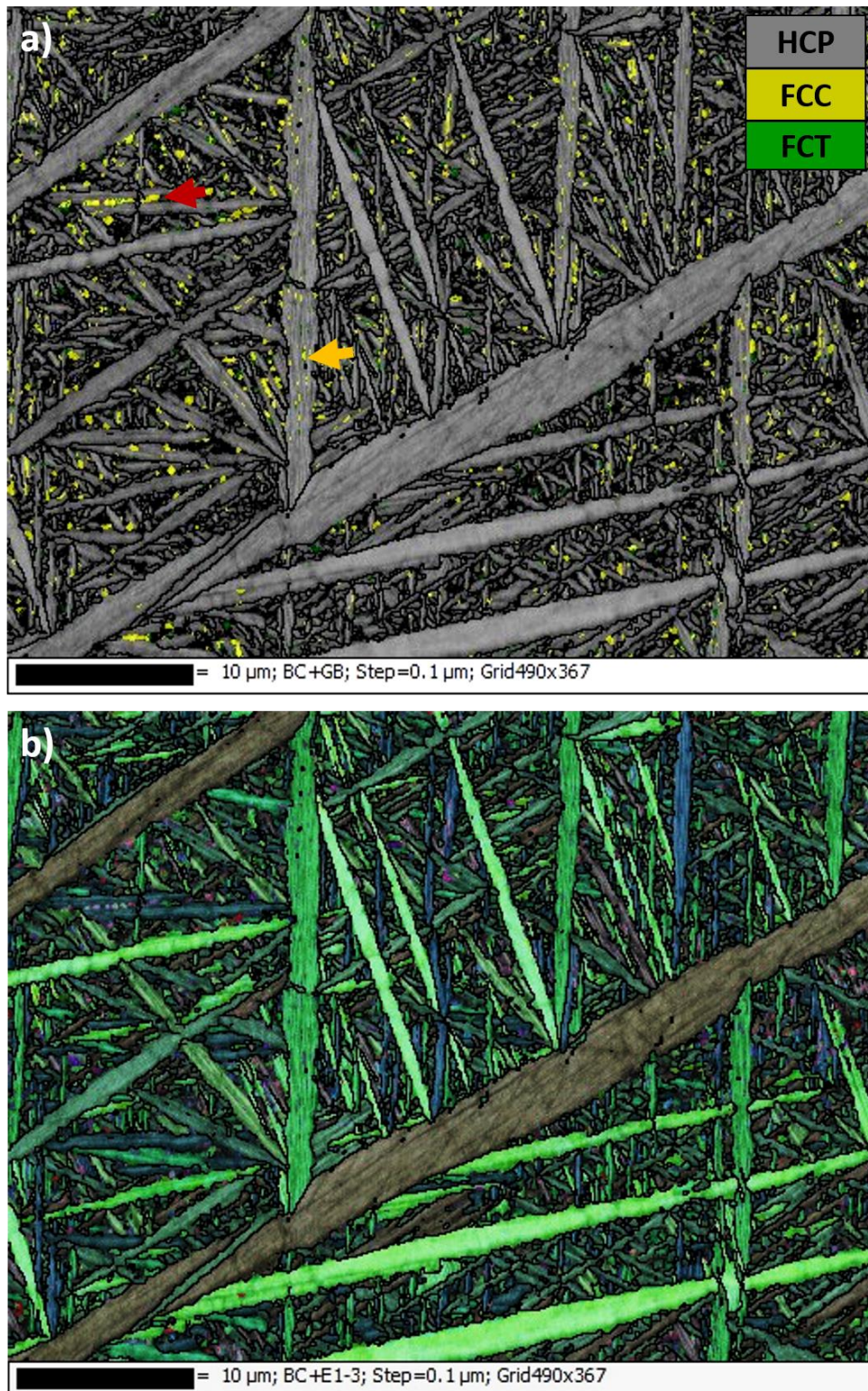


Figure 7. 6: EBSD a) phase and b) Euler colour maps of the aged THDP sample. Image a) shows that aging martensite nucleated refined HCP alpha and FCC, FCT hydrides. Linear hydrides (red arrow) nucleated adjacent to HCP plates and nanobanded hydrides (orange arrow) nucleated within HCP plates. Image b) shows that the nucleated HCP alpha variants retained the orientation and morphological configurations of the tempered martensite plates. Nanobanded hydrides within tempered martensite plates also retained the orientation of the parent plate. The black lines demarcate grains with a minimum misorientation of 15° .

7.3 Phase composition in the aged THDP microstructure

Elemental partitioning is a normal component of Ti-6Al-4V martensite decomposition and it occurs in both hydrogen tempered and non-hydrogen tempered martensite.^{116, 117} However, hydrogen tempered martensite has a uniquely extensive Al partitioning which increases the degree of Al enrichment. This is because alloyed hydrogen stabilises a metastable BCC phase which increases Al partitioning towards tempered martensite plates. It also precipitates hydrides which partition Al, intensifying its enrichment in neighbouring regions.

7.3.1 Al partitioning towards tempered martensite plates

Figure 7.7 a-c) shows a) a HAADF STEM micrograph and complementary EDS maps which compare the b) Al and c) V distribution in the tempered martensite plates and their interplate regions. The aged THDP microstructure has Al rich tempered martensite plates and an Al lean (or V rich) interplate region. This means that Al partitioned towards the HCP plate and V partitioned towards the interplate regions during aging. The degree of Al partitioning in hydrogen tempered martensite is enhanced by the hydrogen stabilised metastable BCC phase. The metastable BCC phase decomposes to nucleate hydrogen saturated alpha and ultimately hydride precipitates.

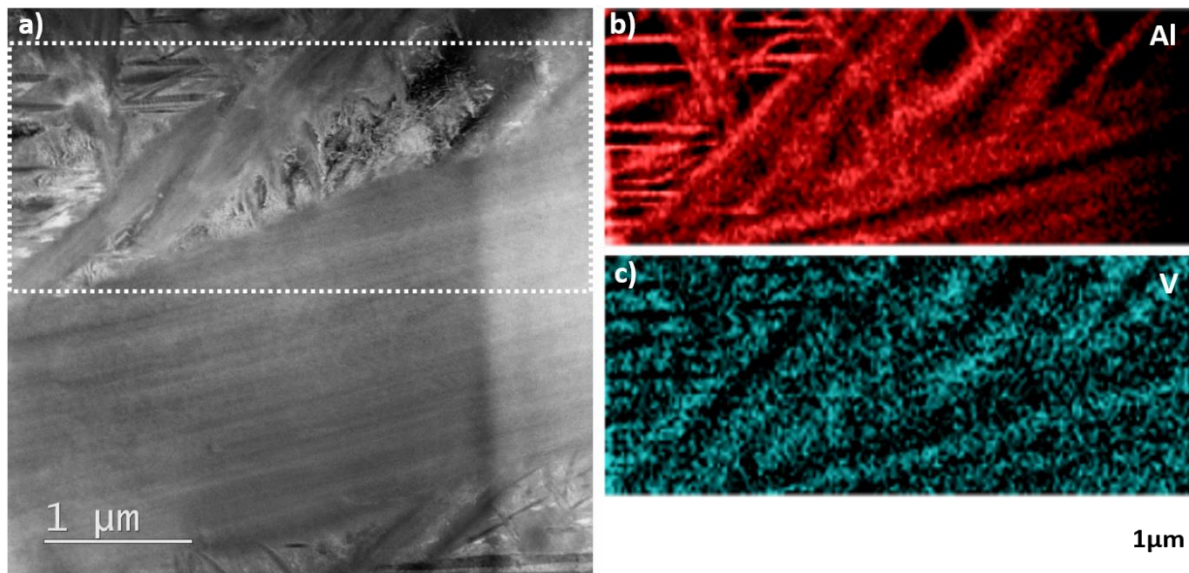


Figure 7. 7: a) HAADF STEM of the aged THDP sample and complementary EDS b) Al and c) V maps obtained from the highlighted area in a). Aging partitioned Al to the acicular plates and vanadium to the interplate regions.

Figure 7.8 a-c) shows a) bright and b) dark field STEM micrographs of tempered martensite highlighting the region of interest in red. Image c) is an atomic resolution HAADF STEM micrograph of the region of interest. Atomic Z-contrast in b, c) reiterates that tempered martensite plates are rich in aluminium whilst the interplate regions are rich in vanadium. It also shows that tempered martensite plates are bordered by regions which are significantly enriched in vanadium.

Figure 7.8 d-f) show [0001] zone axis Fourier transforms of d) the Al rich tempered martensite plate and e) its bordering V rich region. The Fourier transforms are indexed in f). The lattice parameters of a standard Ti-6Al-4V [0001] zone axis HCP crystal are 0.29nm in the $[\bar{1}2\bar{1}0]$, $[2\bar{1}\bar{1}0]$ directions and 0.25nm in the $[1\bar{1}00]$ direction. In comparison, the Fourier transforms of the tempered martensite plate and its bordering V rich region have [0001] HCP lattice parameters of 0.23nm in the $[\bar{1}2\bar{1}0]$, $[2\bar{1}\bar{1}0]$ directions and 0.25nm in the $[1\bar{1}00]$ direction.

The Fourier transforms show that the crystal structure of the Al rich plate is similar to its adjacent or bordering V rich region. However, the Al rich plate has additional superlattice reflections with lattice parameters 0.45nm in the $[1\bar{1}00]$ direction. The superlattice reflections confirm that the Al enrichment (in the Al rich plate) stabilised Ti_3Al precipitates. Comparatively, its adjacent V rich region has no superlattice reflections and is therefore HCP alpha phase. The Fourier transforms also show that the lattice parameters of the Al rich plate and its bordering V rich region are slightly larger than the standard Ti-6Al-4V [0001] zone axis HCP crystal. This means that the former crystal is expanded possibly due to residual hydrogen.

In summary, **Figure 7.6 a)** showed linear hydride precipitates which are adjacent to tempered martensite plates. **Figures 7.7 a-c)** showed that tempered martensite plates are rich in Al and the interplate region is rich in vanadium. **Figure 7.8 b, c)** showed that the Al rich tempered martensite plates have adjacent or bordering regions which are significantly enriched in vanadium. **Figure 7.8 d-f)** showed that the Al enrichment in the tempered martensite plates stabilised Ti_3Al precipitates.

This means that, during hydrogen tempering vanadium partitioned towards the BCC interplate region and aluminium partitioned towards the HCP plates. The metastable BCC

subsequently decomposed to nucleate hydrogen saturated alpha and ultimately hydride precipitates. Hydride precipitates nucleated at tempered martensite plate boundaries to form adjacent (or bordering), linear hydride precipitates. The hydrides partitioned Al and this extensively enriched adjacent tempered martensite plates with Al to critical concentrations that stabilised Ti_3Al .

The Fourier transform of the V rich region that is adjacent to (or borders) tempered martensite plates (**Figure 7.8 e**) shows an expanded [0001] zone axis HCP crystal structure. This indicates that linear hydrides inadvertently decomposed to HCP phase after the electron transparent sample was exposed to high vacuum. However, the expanded HCP crystal lattice indicates residual dissolved hydrogen. This is possible because hydride decomposition occurs in two stages which are determined by the amount of dissolved hydrogen. The $Ti-H_2$ hydride decomposes to $Ti-H_x$ at hydrogen concentrations between ($0.7 < x < 1$) and ultimately alpha phase after full hydrogen escape.⁹⁴ The expanded HCP crystal is therefore at a transient dehydrogenated state and its residual hydrogen content is not sufficient to stabilise hydrides. Since the room temperature kinetics do not sufficiently support Al and V diffusion, hydrides decomposed to a transient V rich alpha.

Selected area diffraction (SAD) also confirmed Ti_3Al in the Al rich tempered martensite plates and HCP alpha in the V rich interplate regions. **Figure 7.9** is a bright field TEM montage of aged THDP microstructures. It highlights SAD analysed regions R1-R6 and their complementary SAD patterns (R1-R6). The SAD regions R1-R2 encapsulate V rich interplate regions whilst SAD regions R4-R6 encapsulate Al rich tempered martensite plates.

In **Figure 7.9**, the selected area diffraction patterns from R1, R2 confirm alpha phase at zone axis $[11\bar{2}3]$. The presence of V rich alpha in the interplate region confirms that a V rich metastable beta decomposed to V rich alpha during aging. The beta phase dissolves more hydrogen (up to 40 at.% H) when compared to alpha phase which dissolves up to 8 at.% H.^{8, 43, 91} This is because hydrogen occupies tetrahedral sites; the BCC crystal has more tetrahedral sites (12) when compared to the HCP crystal which only has (4).¹¹⁸ Therefore metastable beta transformed to V rich, hydrogen saturated alpha and ultimately V rich hydrides.

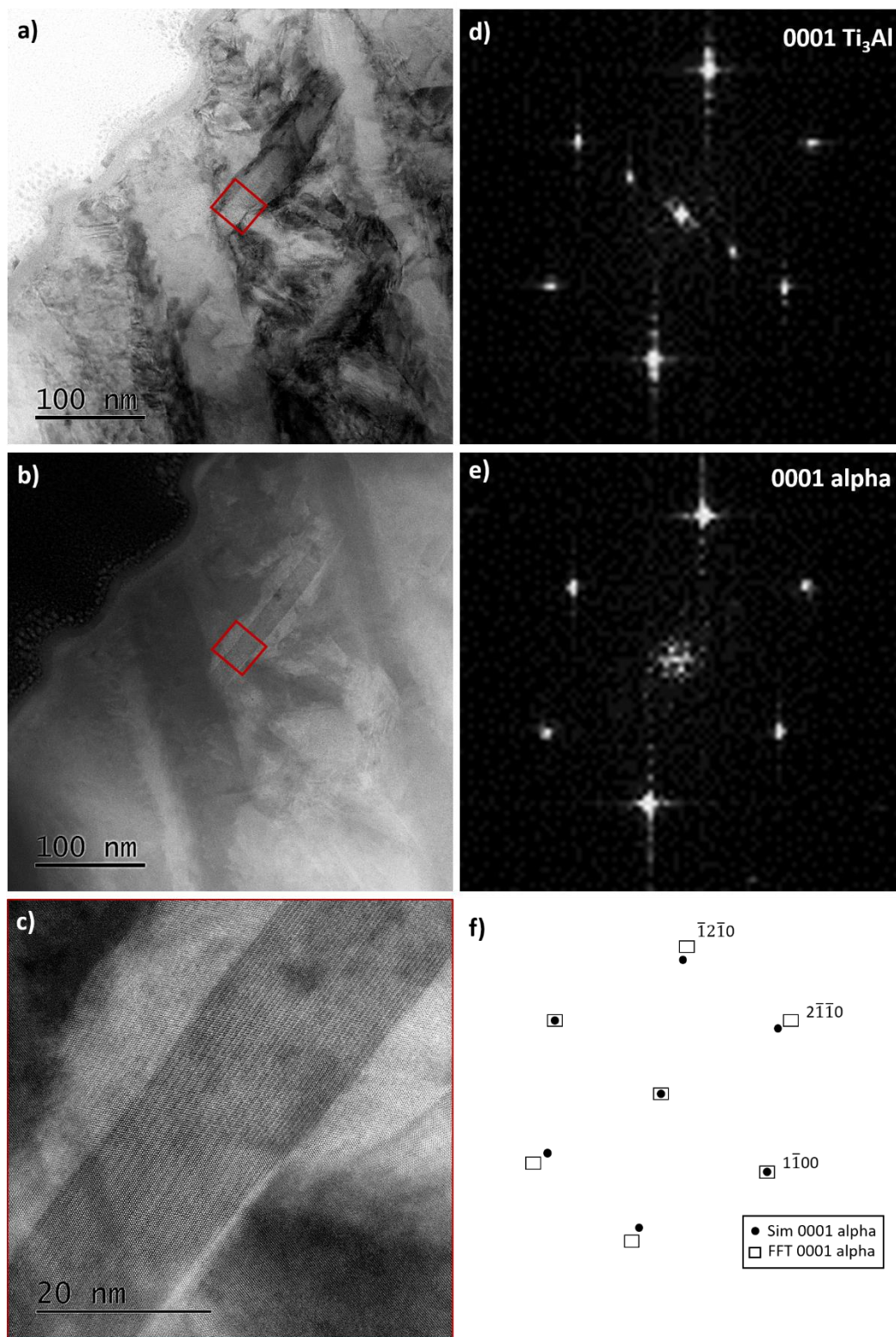
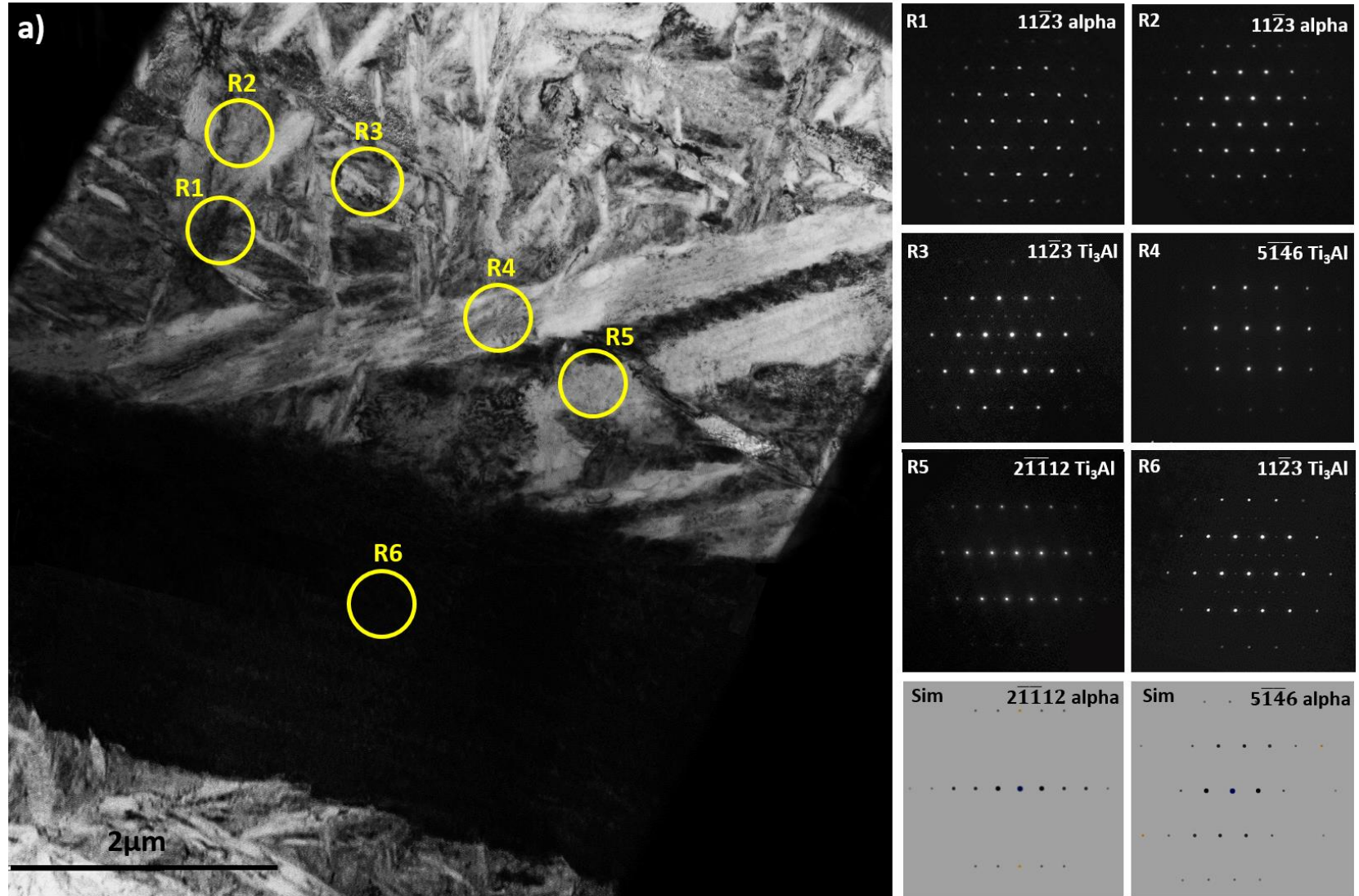


Figure 7. 8: a) bright and b) dark field STEM highlighting (in red) a tempered martensite plate and its adjacent regions. Image c) is an atomic resolution HAADF STEM of the highlighted region in a) showing Al rich (dark) atomic columns in the tempered martensite plate and V rich (bright) atomic columns in its adjacent regions. Images d, e) are [0001] zone axes fast Fourier transforms of the d) Al rich and e) V rich regions. The superlattice reflections in d) confirm Ti_3Al precipitates in the Al rich tempered martensite plates. Image f) shows that the [0001] FFT's in d) and e) are expanded when compared to the standard Ti-6Al-4V [0001] HCP crystal.



7.3.2 Al partitioning within acicular plates

Aluminium not only partitioned towards martensite plates but it also partitioned within plates to form periodic Al rich, V rich nanobands. The partitioning of Al towards martensite plates combined with the partitioning of Al within martensite plates resulted in extensive Al enrichment to critical levels that stabilised Ti_3Al in Al rich nanobands.

In **Figure 7.9**, selected area diffraction patterns from regions R3-R6 confirmed Ti_3Al precipitates in tempered martensite plates at zone axes $[11\bar{2}3]$, $[5\bar{1}\bar{4}6]$, $[2\bar{1}\bar{1}12]$ respectively. The absence of superlattice reflections in the simulated alpha $[5\bar{1}\bar{4}6]$ and $[2\bar{1}\bar{1}12]$ zone axis diffraction patterns confirms the experimental SAD patterns to be Ti_3Al precipitates and not alpha phase.

Selected area diffraction (SAD) analysis confirmed Ti_3Al precipitates in tempered martensite plates. However, it could not accurately characterise the nanobanded morphology because of its spatial resolution limits. Selected area diffraction presented collective diffraction information from the Al rich and V rich nanobands. The diffraction information from Al rich nanobands had superlattice reflections which overshadowed the diffraction information from Al lean nanobands. Therefore SAD analysis of tempered martensite plates consistently confirmed Ti_3Al precipitates. The nanobanded morphology was then characterised by atomic resolution microscopy.

Figure 7.10 a-b) shows a) a HAADF STEM micrograph highlighting acicular plate R6 (see **Figure 7.9**). Atomic Z-contrast in **Figure 7.10 a)** shows elemental partitioning within the tempered martensite plate R6 as periodic Al rich (dark), V rich (bright) nanobands. The complementary EDS map in b) confirms the periodic, nanoscale partitioning of aluminium within the tempered acicular plate.

Figure 7.10 c) is an atomic resolution HAADF STEM micrograph of the nanobands in R6. It shows Al rich (dark) and V rich (bright) atomic columns which are approximately 20nm in width. Image c) also shows that the Al rich, V rich nanobands have a coherent interface.

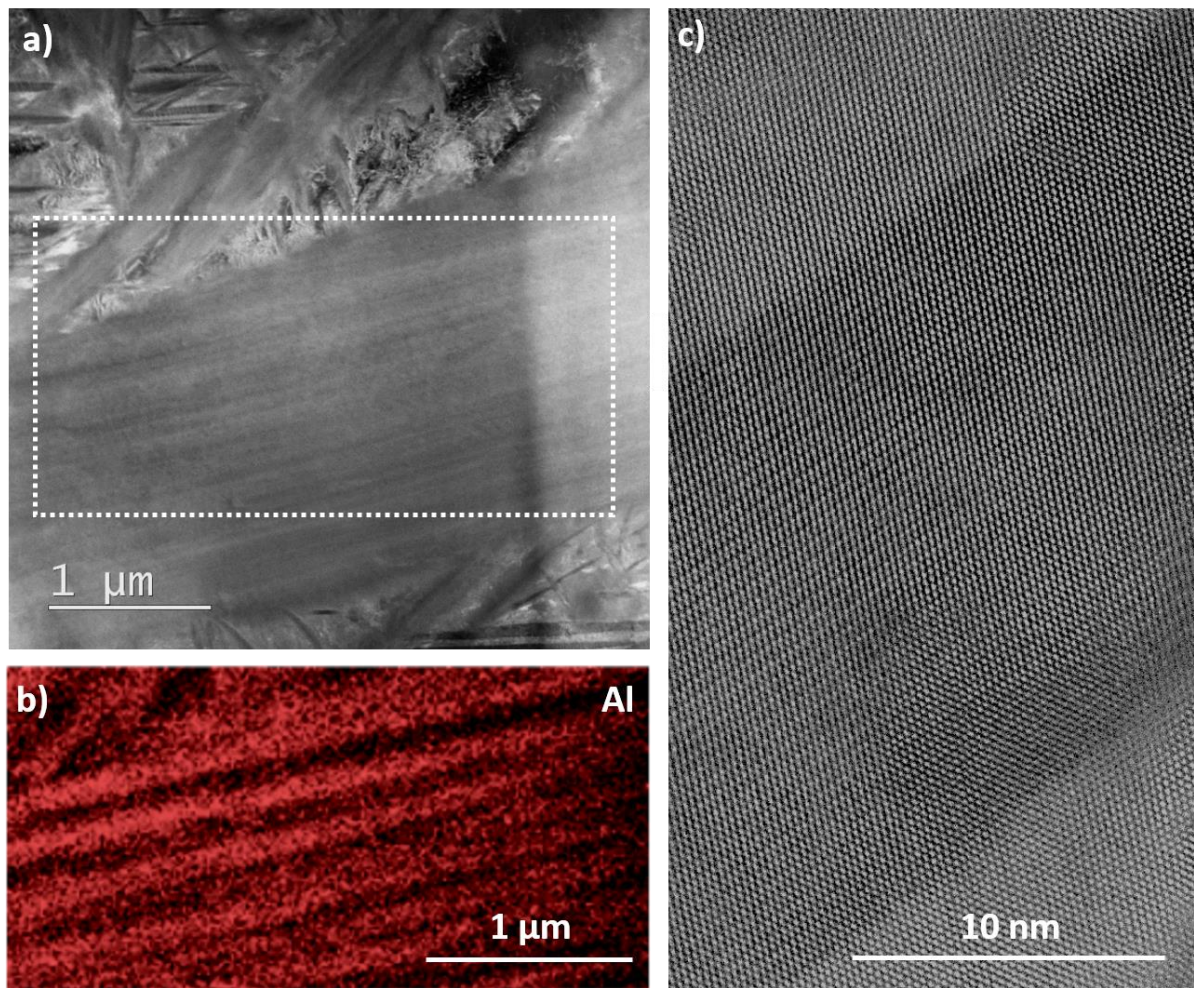


Figure 7. 10: a) HAADF STEM micrograph highlighting the tempered martensite plate R6 (see **Figure 7.9**) and b) a complementary EDS map attained from mapping the highlighted region. Images a) and b) show a periodic, nanoscale variation in aluminium (Al) and vanadium (V) composition which occurs as Al rich, Al lean (or V rich) nanobands within acicular plate R6. Image c) also shows that the interface between the Al rich, Al lean (or V rich) nanobands is coherent.

7.3.3 The degree of Al enrichment in nanobanded martensite plates

The partitioning of elements is a normal part of martensite decomposition. Hydrogen intensifies the extent of Al partitioning and enrichment to promote Ti_3Al precipitation at short aging times (within 3 hours of aging at 580°C). Similarly aging non-hydrogenated martensite for 3 hours at 580°C does not cause extensive Al enrichment which stabilises Ti_3Al as described in **Section 6.3.2**.

Figure 7.11 a-c) shows high resolution a) bright field TEM and b) HAADF STEM micrographs of nanobands within a tempered martensite plate. Image b) highlights regions of interest R7 and R8 and image c) is a complementary EDS map showing Al partitioning in region R8. Atomic Z-contrast in **Figure 7.11 b)** highlights periodic Al rich (dark), Al lean or V rich (bright) nanobands. The periodic Al enrichment is confirmed by the complementary EDS map in **Figure 7.11 c)**.

Figure 7.12 a, b) shows high resolution HAADF STEM micrographs of regions a) R7, b) R8 which highlight EDS point analyses 1-4. The degree of Al enrichment at points 1-4 is presented in **Figure 7.12 c)**. The Al rich nanobands have up to 18 at.%Al and the Al lean (or V rich) nanobands have at most 6 at.%Al. The EDS points 1 and 2 also show a sharp transition in Al content (of up to 12 at.%Al) at adjacent nanobands which are approximately 50nm apart.

An aluminium concentration of 18 at.%Al is expected to stabilise Ti_3Al . The presence of Ti_3Al precipitates was confirmed from Fourier transforms of the Al rich, Al lean (or V rich) nanobands in **Section 7.4**.

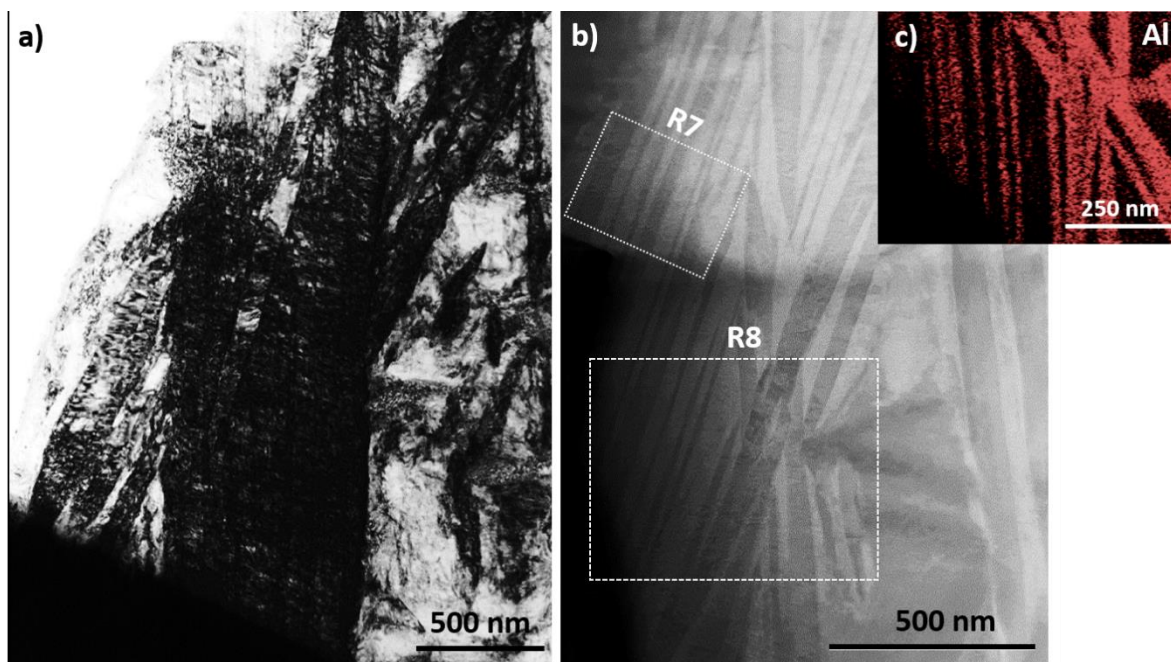


Figure 7.11: a) Bright field TEM and corresponding b) HAADF STEM of a tempered martensite plate highlighting regions R8, R9. Image c) is a complementary EDS map attained from region R8. The dark contrast nanobands (b) uncover the periodic, nanoscale variation in Al composition within the tempered plate shown in (a). This periodic variation in Al content is confirmed by the complementary EDS map of R8 in image c).

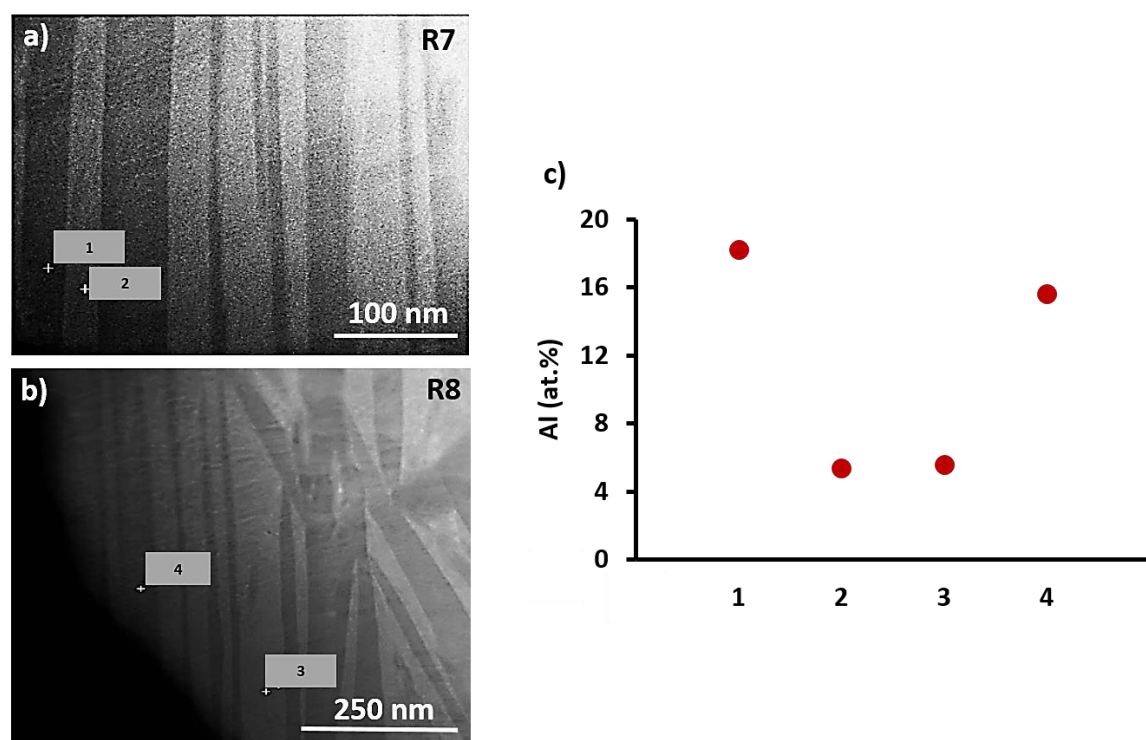


Figure 7.12: High resolution HAADF STEM micrographs of nanobanded regions a) R7 and b) R8 highlighting EDS point analysis (1-4) which was performed on Al rich (dark), Al lean (or V rich) bright nanobands. The degree of Al enrichment at Al rich nanobands is up to 18 at.%Al whilst the Al lean nanobands have at most 6 at.%Al. The composition difference at adjacent nanobands (EDS points 1 and 2) is up to 12 at.%Al.

7.4 Crystal structure of nanobanded regions within tempered acicular plates

The crystal structure of the Al rich, Al lean (or V rich) nanobands within tempered martensite acicular plates was viewed from the [0001] zone axis.

Figure 7.13 a) shows a) bright field STEM micrograph of a nanobanded acicular plate. **Figure 7.13 b)** is a high magnification HAADF STEM micrograph of the yellow highlighted nanobanded region in a). **Figure 7.13 c)** is an atomic resolution HAADF STEM micrograph of the red highlighted region in b) showing Al rich (dark) and V rich (bright) atomic columns.

Figure 7.13 d, e) shows the corresponding FFT patterns of the d) Al rich and e) V rich nanobands. In **Figure 7.13 f)**, the standard Ti-6Al-4V [0001] zone axis HCP crystal is superimposed on the [0001] zone axis FFT pattern to illustrate the difference in lattice parameters. The lattice parameters of a standard Ti-6Al-4V [0001] zone axis HCP crystal are 0.29nm in the $[\bar{1}2\bar{1}0]$, $[2\bar{1}\bar{1}0]$ directions and 0.25nm in the $[1\bar{1}00]$ direction. Comparatively, the Fourier transforms have [0001] HCP lattice parameters of 0.23nm, 0.22nm in the $[\bar{1}2\bar{1}0]$, $[2\bar{1}\bar{1}0]$ directions and 0.25nm in the $[1\bar{1}00]$ direction.

The Fourier transforms show that the crystal structure of the Al rich nanoband is similar to its adjacent V rich nanoband. However, the Al rich nanoband has additional superlattice reflections. The superlattice reflections confirm that the Al enrichment (in the Al rich nanoband) stabilised Ti_3Al precipitates. The Fourier transforms also show that the Al rich, or V rich nanobands have a coherent HCP crystal structure which has the same crystallographic orientation. Therefore Fourier transforms confirm the Al rich, V rich nanobands to be periodic Ti_3Al , alpha phase respectively.

In **Figure 7.13 f)**, the [0001] zone axis Fourier transforms of the Al rich, V rich nanobands have an expanded HCP crystal structure which indicates residual dissolved hydrogen. The contribution of hydrogen to the nanobanded morphology is discussed in **Section 7.5**.

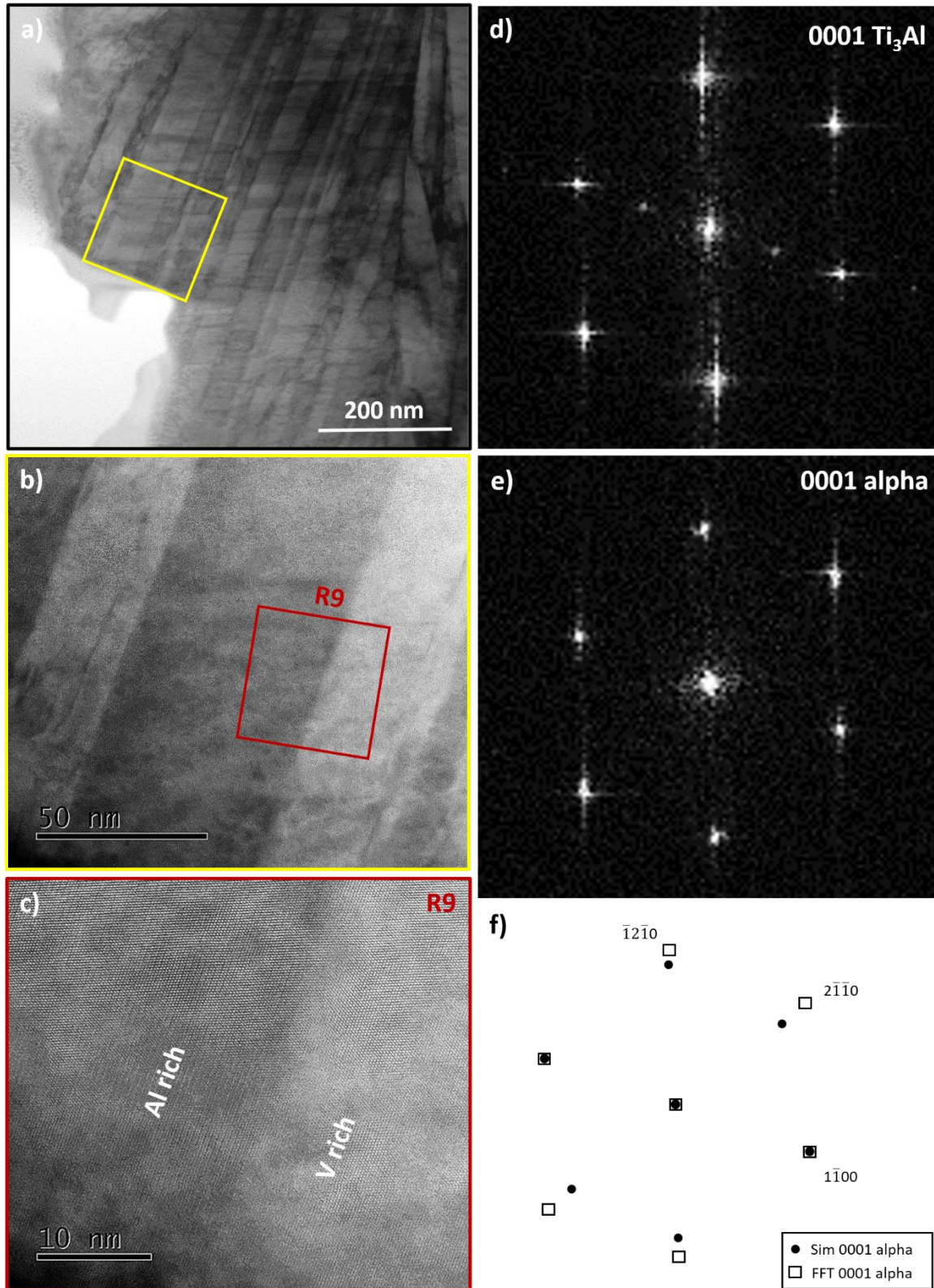


Figure 7. 13: a) Bright field STEM highlighting (in yellow) nanobands within a tempered martensite plate. Image b) is a high resolution HAADF STEM micrograph of the yellow region in a) and it highlights the region of interest R9 in red. Image c) is an atomic resolution c) HAADF STEM micrograph of R9 showing atomic columns of Al rich (dark) and Al V rich (bright) nanobands. The [0001] zone axes Fourier transforms of the Al rich and V rich nanobands are shown in d) or e) respectively and they are indexed in image f).

7.5 The contribution of hydrogen to the nanobanded morphology

The nanobanded morphology is a typical hydride morphology, it occurs when hydride precipitates configure to a particular nucleation interface. It has been observed within hydrogen tempered orthorhombic martensite plates after nucleating from twin interfaces¹⁶ or stacking faults.⁵¹ It has also been observed in equilibrium (non-martensitic) Ti-6Al-4V, which was beta decomposed in the presence of alloyed hydrogen, where nanobands nucleated at alpha grain interfaces.^{50, 51}

In this work, the nanobanded morphology was observed within hydrogen tempered hexagonal martensite plates after nucleating from nanosized slip bands. The nanosized slip bands are a lattice invariant deformation that occurs within martensite plates to accommodate Bain strain (see **Figure 7.2**). Aging at 580°C decomposed martensite to nucleate hydrogen saturated alpha and ultimately hydrides. Nanobanded hydride precipitates nucleated at nanosized slip bands within tempered martensite plates. They coherently grew through a supply of hydrogen from surrounding hydrogen saturated alpha.^{50, 51} In the same light, aluminium and vanadium respectively partitioned towards the growing alpha and hydride nanobands. The hydride and the alpha nanobands grew through coherent epitaxial growth¹¹⁵ to maintain the orientation of the parent martensite plate.

The partitioning of elements is a normal part of martensite decomposition. Elements typically partition to stabilise specific phases. This partitioning can result in periodic composition fluctuations if the phases are arranged in a periodic, alternate configuration as observed in Ti-Cu martensite.¹¹⁷ Similarly in this work, the nanobanded morphology has a periodical variation in composition because Al and V respectively partitioned towards a periodic, alternate alpha and hydride phase configuration.

Hydrogen is not responsible for the observed partitioning of elements, but it contributes to the degree of Al enrichment in the Al rich nanoband. This occurs because hydrogen stabilises hydride nanobands (Ti-H or Ti-H₂), which partition Al to extensively enrich adjacent alpha nanobands with Al. This extensively enriches adjacent alpha nanobands with Al to critical levels that stabilise Ti₃Al.

Exposure to vacuum inadvertently dehydrogenated the electron transparent sample. This decomposed hydride nanobands to V rich alpha nanobands. Consequently, atomic resolution TEM in **Figure 7.13 f)** confirms the nanobanded morphology to be periodic, alternating Al rich and V rich HCP alpha phase.

However, Fourier transforms of the Al rich, V rich nanobands in **Figure 7.13 f)** show that they have an expanded [0001] zone axis crystal structure. This indicates that there could be residual dissolved hydrogen that is expanding the HCP crystal. This is possible because hydride decomposition occurs in two stages which are determined by the amount of dissolved hydrogen. The Ti-H_2 hydride decomposes to Ti-H_x at hydrogen concentrations between ($0.7 < x < 1$) and ultimately alpha phase after full hydrogen escape.⁹⁴

The expanded HCP crystal is therefore at a transient dehydrogenated state and its residual hydrogen content is not sufficient to stabilise hydrides. The room temperature hydride decomposition does not support significant element diffusion and therefore the hydride decomposes to a transient V rich alpha. The V rich alpha nanoband is identified as a hydride landmark after hydride decomposition.

7.6 Elements of hydrogenation-disproportionation in the aged THDP microstructure

The evolution of plate martensite and metastable beta in the THDP treated sample is comparable to its THP treated counterpart in **Chapter 6**. Therefore, the previously discussed hydrogenation-disproportionation half reactions for plate martensite (**Equation 10**) and metastable beta (**Equation 11**) are applicable to the THDP treated microstructure.

Chapter 7 adds atomic resolution information which enhances or validates **Equations 10** and **11**. For instance, **Chapter 6** inferred that linear hydrides partition aluminium when formulating **Equation 11** (see **Section 6.7.1**). **Chapter 7** validates that the latter is true; linear hydrides partition Al to neighbouring HCP regions where the consequent Al enrichment stabilises Ti_3Al phase. Moreover, **Chapter 7** also validates **Equation 10** by showing that hydride nanobands nucleate at linear crystal imperfections within plate martensite.

7.7 Grain and morphology refinement in the THDP 675 microstructure

To produce the THDP 675 microstructure, as-cast Ti-6Al-4V was hydrogenated (to 20 at.%H), hot deformed (true strain 1.6 at 10s^{-1} rate), recrystallized (at 900°C for 15 minutes) plus quenched, aged (at 580°C for 3 hours) and dehydrogenated (at 675°C for 3 hours) Ti-6Al-4V.

7.7.1 Submicron grain refinement

Figure 7.14 a-c) compares the grain size of a) as-cast Ti-6Al-4V to the THDP 675 microstructure. The black lines in **Figure 7.14 a)** show that the as-cast Ti-6Al-4V microstructure has a coarse prior beta grain size (of up to $2000\text{ }\mu\text{m}$ grain diameters), Widmanstätten (A) and basketweave (B) morphologies. The Widmanstätten morphology results from the Widmanstätten growth that occurs after slow cooling past the beta transus temperature. Alpha phase initially nucleates at the prior beta grain boundaries to form grain boundary alpha which delineates the coarse grained structure of the as-cast Ti-6Al-4V microstructure. The basketweave morphology results from the re-nucleation of alpha grains that occurs after it becomes more energy efficient to nucleate new alpha grains than grow existing ones. The THDP 675 treatment refines the grain size from $2000\text{ }\mu\text{m}$ grain diameters to submicron grain diameters as shown in **Figure 14 b, c)**.

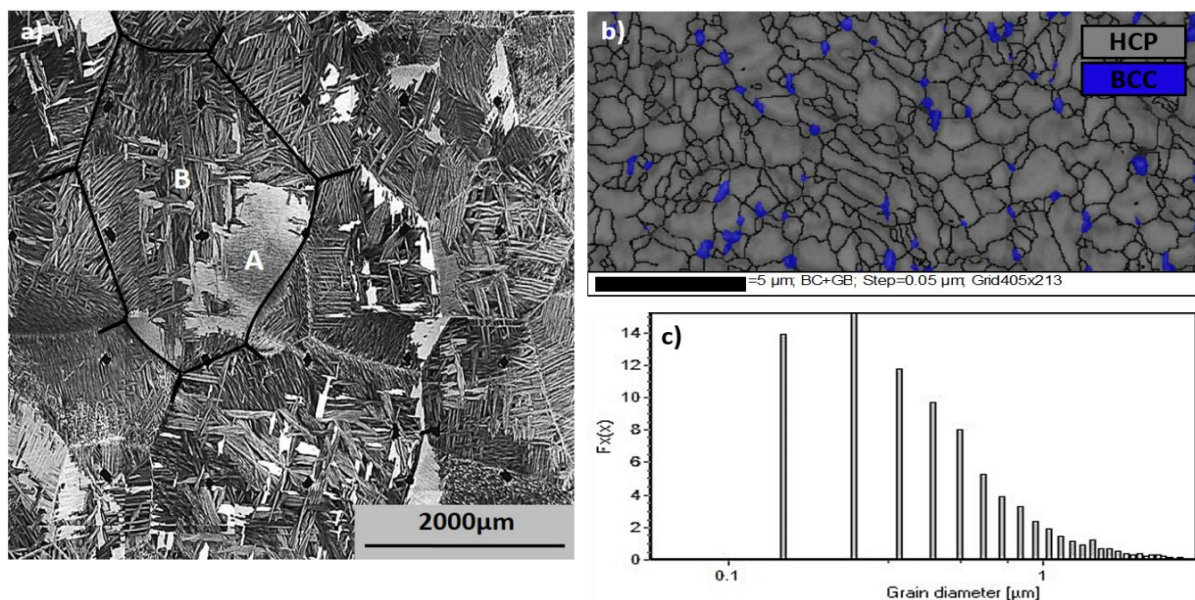


Figure 7. 14: Grain size comparison between a) as-cast Ti-6Al-4V and the b, c) refined THDP 675 microstructure. The black lines in b) demarcate high angle grain boundaries with a minimum misorientation of 15° . The as-cast Ti-6Al-4V microstructure has coarse prior beta grains (of diameter $2000\text{ }\mu\text{m}$), Widmanstätten (A) and basketweave (B) morphologies. The grain size is refined to submicron level after THDP treatment.¹¹⁹

7.7.2 Morphology refinement

Figure 7.15 is an Euler colour map of the submicron grained THDP 675 microstructure. **Figure 7.15** shows that the morphology of as-cast Ti-6Al-4V was refined from Widmanstätten to indentation mark or triangular morphologies. The indentation mark or triangular morphologies are 2 or 3 variant cluster morphologies that result from self-accommodation of martensite plates and alpha variants during quenching and aging.

Self-accommodation presents an indelible influence on the extent of morphology refinement that can be achieved in THDP treated Ti-6Al-4V. This is because the indentation mark or triangular morphologies are retained by the submicron grains that nucleate after dehydrogenation. Self-accommodation promotes nucleation of alpha variants that result in optimum self-accommodated groupings.¹¹⁴ In this instance, the optimum self-accommodated groupings are configured to the triangular or indentation mark morphologies. Therefore the nucleated submicron grains have self-repeating patterns of variant selected alpha that is configured to the latter morphologies as shown in **Figure 7.15**.

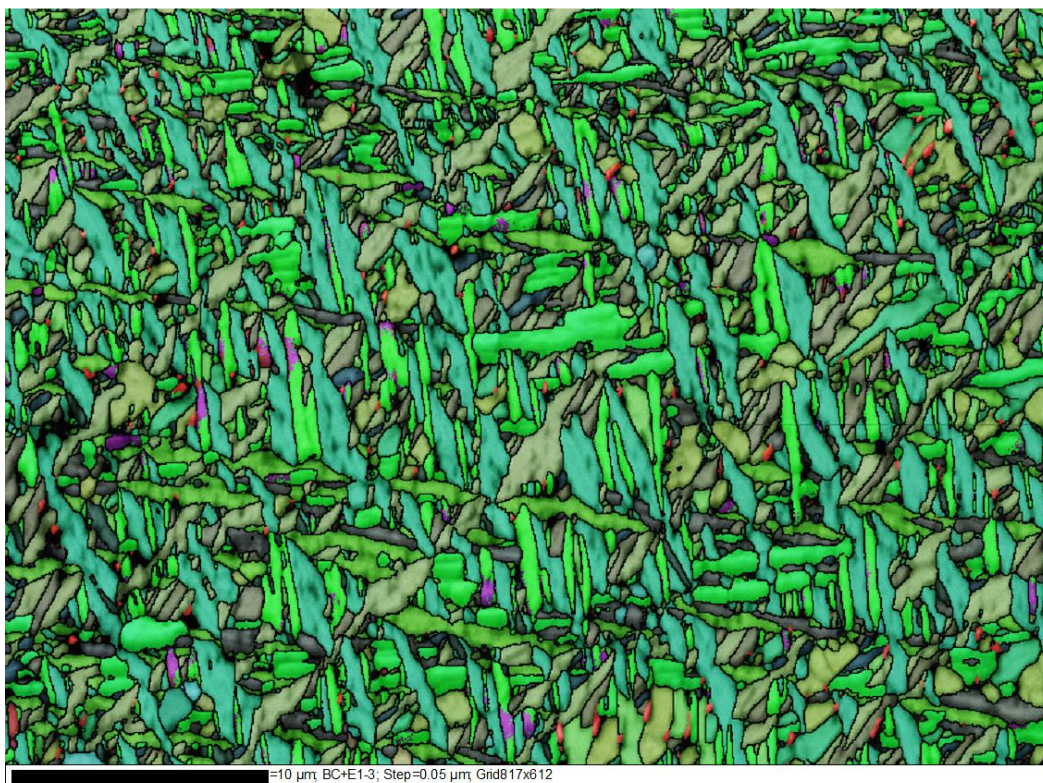


Figure 7. 15: Euler colour map of the THDP 675 sample showing self-accommodated groupings of selected alpha plate variants in the submicron grained microstructure. The self-accommodated groupings are configured to the indentation mark or triangular morphologies. The black lines demarcate grains with a minimum misorientation of 15°.

7.8 Recombination in the THDP 675 microstructure

Figure 7.16 a-b) shows a) HAADF STEM micrograph of the THDP 675 sample highlighting EDS point analyses 1-14 which are presented in b). **Figure 7.16 b)** show that the degree of aluminium enrichment in the THDP 675 sample is up to 24 at.%Al.

Figure 7.17 a-c) shows a TKD phase map of the THDP 675 sample highlighting HCP alpha grains 1 and 2 and their corresponding EDS b) aluminium (Al) and c) vanadium (V) maps. The THDP 675 sample has alpha (HCP) and beta (BCC) phases which are typically enriched in Al and V respectively. However, its HCP alpha phase also has retained Al rich clusters. The Al rich clusters were caused by fine hydride precipitates which partitioned Al to neighbouring regions. Dehydrogenating at 675°C retained the Al rich clusters in the THDP 675 microstructure.

Selected area diffraction (SAD) confirmed Ti_3Al precipitates in the THDP 675 sample. **Figure 7.18 a, b)** shows bright field TEM micrographs of grains 1,2 and their corresponding SAD patterns attained from Al rich clusters (R10, R12) and their neighbouring Al lean regions (R11, R13). The R10 and R12 SAD patterns confirm Ti_3Al precipitates in the Al rich clusters at zone axes $[21\bar{3}0]$ and $[10\bar{1}0]$ respectively. Similarly the R11 and R13 diffraction patterns confirm their neighbouring regions to be alpha phase at zone axes $[21\bar{3}0]$ and $[10\bar{1}0]$ respectively. The SAD patterns also confirm that the orientation of Ti_3Al precipitates is coherent with their parent alpha grains.

The submicron grained microstructure of the THDP 675 microstructure promises extensive strength improvement as stipulated by the Hall Petch relation. However, the Ti_3Al precipitates threaten the tensile performance of the submicron grained microstructure. Increasing the dehydrogenation temperature to 750°C significantly reduces the volume fraction of Ti_3Al to extents that eliminate Ti_3Al embrittlement. However, this may also reduce the strength of THDP 675 samples because of the combined effect of martensite softening and grain coarsening.

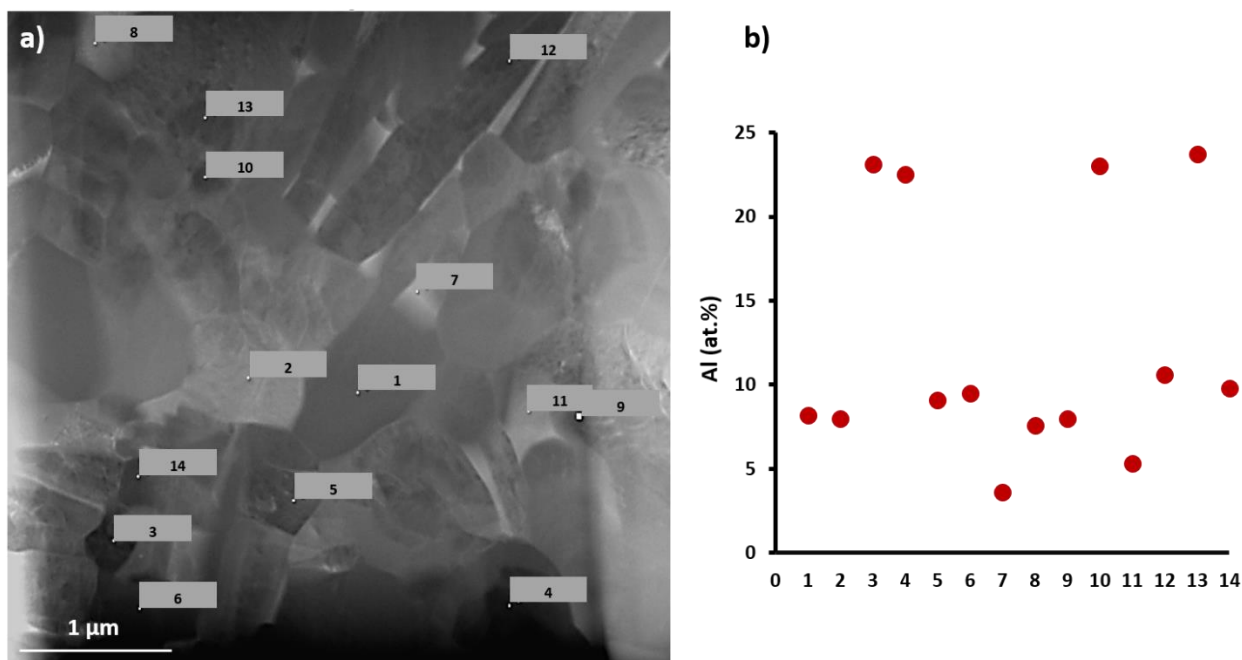


Figure 7. 16: a) HAADF STEM micrograph of the THDP 675 microstructure highlighting EDS point analyses 1-14 which are presented in b). Dehydrogenating THDP treated microstructures at 675°C retains Al rich clusters where the Al content is up to 24 at.%Al.¹¹⁹

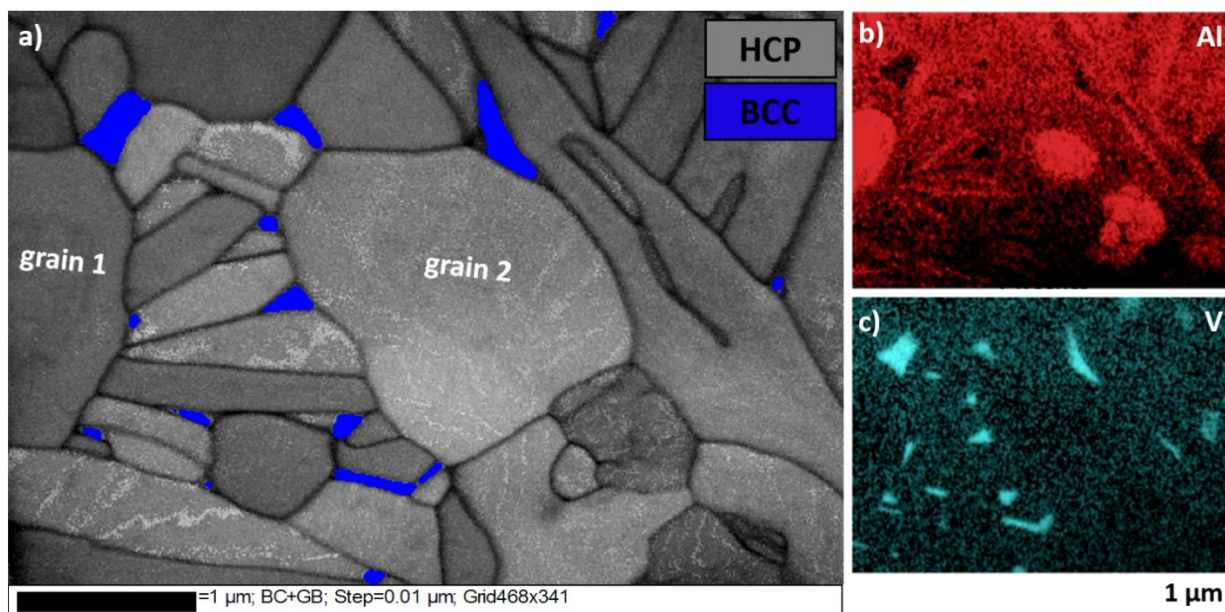


Figure 7. 17: a) TKD phase and corresponding EDS b) aluminium (Al), c) vanadium (V) maps of the THDP 675 microstructure. In a), the THDP 675 microstructure has alpha (grey-HCP) and beta (blue-BCC) phases. The BCC phase is primarily rich in vanadium and the HCP phase has retained Al rich clusters.

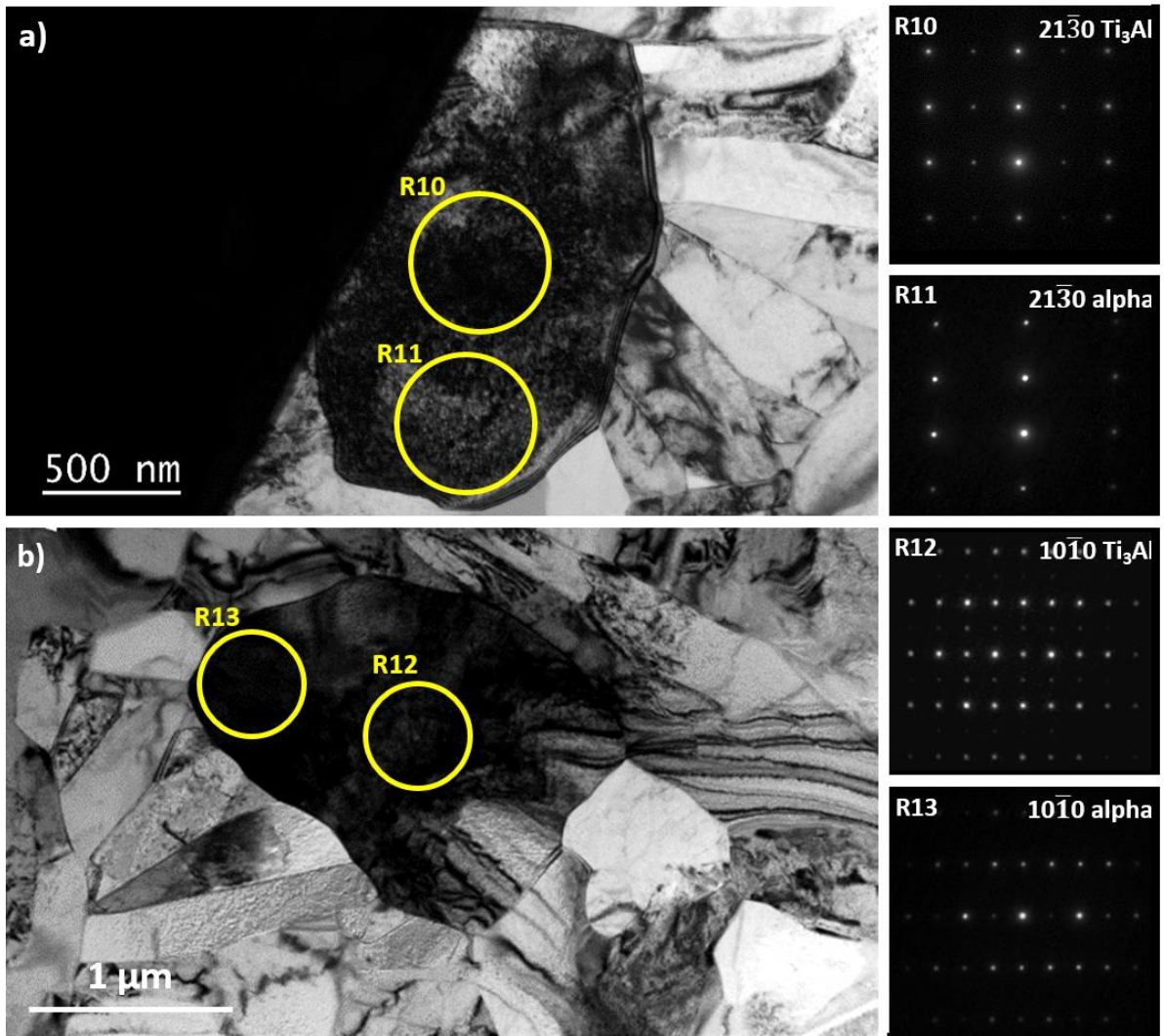


Figure 7. 18: a, b) bright field TEM highlighting regions R10-R13 and their corresponding SAD patterns R10-R13. Image a) highlights the SAD analysed regions of grain 1 (in **Figure 7.17**) where R10 is Al rich and R11 is Al lean. Similarly image b) highlights the SAD analysed regions of grain 2 (in **Figure 7.17**) where R12 is Al rich and R13 is Al lean. The complementary SAD patterns confirm Ti_3Al at Al rich regions (R10 and R12) and alpha at Al lean regions (R11 and R13) at the zone axes $[21\bar{3}0]$ and $[10\bar{1}0]$. The SAD patterns also show that the orientation of the Ti_3Al precipitates is coherent with the parent alpha grain.

7.9 Summary of thermohydrogen and deformation processing (THDP)

As-cast Ti-6Al-4V was hydrogenated (to 20 at.%H), hot deformed (true strain 1.6 at 10s^{-1} rate), recrystallized (at 900°C for 15 minutes) plus quenched, aged (at 580°C for 3 hours) and dehydrogenated (at 675°C for 3 hours). Samples were extracted at the quenched, aged and 675°C dehydrogenated stages of the heat treatment to analyse microstructure evolution during THDP treatment.

7.9.1 The recrystallised and quenched THDP microstructure

Recrystallisation and quenching refined the prior beta grain size diameters from $2000\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$ - $20\text{ }\mu\text{m}$. Quenching promoted a partial BCC to HCP martensite plate transformation. The HCP martensite plates had nanosized linear crystal defects (shear bands) caused by the lattice invariant deformation that occurs during martensite transformation. Hydrogen prevented a full BCC to HCP transformation by stabilising some of the high temperature BCC phase as a metastable phase at room temperature. Self-accommodation grouped martensite plate variants to specific configurations that minimised the strain exerted on the non-transformed BCC parent. Variant selection resulted from the nucleation of martensite plate variants that offered optimum self-accomodated groupings. The self-accomodated plate groupings were configured to self-repeating patterns of 2 or 3 variant morphologies known as indentation mark or triangular morphologies respectively.

7.9.2 The aged THDP microstructure

Aging at 580°C decomposed martensite and this occurred through a diffusion controlled partitioning of aluminium and vanadium. Aluminium partitioned towards the acicular plates and within acicular plates. Vanadium partitioned towards the interplate region and within acicular plates. Martensite decomposed to nucleate hydrogen saturated alpha and ultimately hydride precipitates. Fine hydrides, linear hydrides and nanobanded hydrides precipitated in the aged THDP sample. Linear hydrides nucleated at plate boundaries and nanobanded hydrides nucleated at nanosized shear bands within martensite plates. Hydrides partitioned Al and extensively enriched adjacent HCP grains with Al to critical levels that stabilised Ti_3Al phase. The Ti_3Al precipitates were confirmed by SAD of Al rich plates and $[0001]$ zone axis Fourier transforms of Al rich nanobands.

Hydride precipitates decomposed to V rich alpha after electron transparent samples were exposed to vacuum. Selected area diffraction confirmed V rich alpha in the interplate region. Similarly, Fourier transforms of V rich nanobands confirmed an expanded [0001] zone axis HCP alpha crystal. The V rich alpha is a hydride landmark that was retained after inadvertent hydrogen escape and hydride decomposition. The [0001] zone axes HCP crystal was expanded because of a residual hydrogen content that was below the critical hydrogen concentration that stabilises hydrides.

7.9.3 The 675°C dehydrogenated THDP microstructure

Dehydrogenating at 675°C decomposed hydrides and nucleated equilibrium phases, this refined the 2000 μm grain size diameters of as-cast Ti-6Al-4V to submicron level. Self-accommodation configured the morphology of submicron grains to the indentation mark or triangular morphologies. It therefore presented an indelible effect on the degree of morphology refinement that can be achieved from THDP processing.

Dehydrogenating at 675°C retained the Al enriched clusters caused by hydride induced partitioning. The degree of Al enrichment in the Al enriched clusters was up to 24 at.%Al and it was sufficient to stabilise Ti_3Al precipitates in the THDP 675 sample. Selected area diffraction confirmed Ti_3Al precipitates in the Al rich regions of the THDP 675 sample. It also confirmed that Ti_3Al precipitates maintain the orientation of the parent HCP grain.

CHAPTER 8: SUMMARY AND CONCLUSIONS

This thesis investigated the influence of hydrogen on microstructure evolution, grain refinement and mechanical properties (specifically tensile performance). It exposed the unarticulated relationship between hydrogen and Ti_3Al as a gap in literature. This gap has been sustained by the pervasive use of the repeated nucleation framework to account for hydrogen promoted microstructure evolution. In addition, the gap has been perpetuated by the inverse optimisation approach that is employed by grain refinement by temporary hydrogen alloying literature. This approach puts less emphasis on the evolution of grain refinement during hydrogen treatment. Therefore, it does not prioritise detailed microstructure characterisation.

The inverse optimisation approach has consequently promoted literature to rely on singular microstructure characterisation techniques when investigating hydrogen promoted microstructure evolution. However, this thesis demonstrated why complementary analytical techniques are required to successfully characterise Ti_3Al precipitation in hydrogen treated Ti-6Al-4V. For instance, Ti_3Al precipitates in Al enriched clusters that are within HCP grains. These Al enriched clusters can be missed by selected area diffraction analysis if it is not coupled with energy dispersive spectroscopy.

This study showed that it is crucial to account for Ti_3Al precipitation because it can deteriorate the improved property benefits that are expected from hydrogen treated microstructures. Therefore, it hypothesised that the hydrogenation-disproportionation-desorption-recombination (HDDR) framework can account for the evolution of grain refinement in hydrogen treated Ti-6Al-4V. In addition, it hypothesised that grain refinement of Ti-6Al-4V by temporary hydrogen alloying can cause embrittling effects which remain even when hydrogen is fully expelled from the alloy. It then substantiated the latter hypotheses in three hydrogen treatments; hydrogenation-dehydrogenation (HDH), thermohydrogen processing (THP) and thermohydrogen and deformation processing (THDP).

Chapter 4 articulated the intimate relationship between hydrogen and Ti_3Al by showing how hydride induced Al partitioning promotes Ti_3Al precipitation. Consequently, it confirmed elements of hydrogenation-disproportionation in hydrogenated Ti-6Al-4V. The confirmed

elements substantiated that the HDDR framework can account for the evolution of grain refinement in hydrogen treated Ti-6Al-4V. **Chapter 4** also unveiled that hydrides are rich in vanadium (V) and lean in aluminium (Al). The unexpected but observed enrichment of hydrides with vanadium revealed that disproportionation does not proceed through the rejection of vanadium from hydrides as proposed in literature. Instead, hydrides retain vanadium and refined beta grains nucleate from the V rich hydride precipitates during dehydrogenation.

Chapter 5 evaluated the effect of HDDR promoted grain refinement on the tensile performance. It confirmed that a higher degree of embrittlement occurs at lower dehydrogenation temperatures and this is caused by hydrogen induced Ti_3Al precipitates. This substantiated that grain refinement of Ti-6Al-4V by temporary hydrogen alloying can cause embrittling effects which remain even when hydrogen is fully expelled from the alloy.

Chapter 6 similarly evaluated tensile performance in hydrogen tempered martensite. It also highlighted the contribution of hydrogen to tempered martensite evolution. **Chapter 6** showed that substantial embrittlement is caused by martensite formation and subsequent tempering. However, it also highlighted that hydrogen contributes to the tensile performance that is dominated by martensite formation and subsequent tempering. **Chapter 6** reiterated the higher degree of embrittlement that occurs at lower dehydrogenation temperature. This also substantiated that grain refinement of Ti-6Al-4V by temporary hydrogen alloying can cause embrittling effects which remain even when hydrogen is fully expelled from the alloy.

Chapter 7 highlighted the grain and morphology evolution that occurs during the transient stages of the THDP treatment. It emphasised the extensive degree of grain and morphology refinement that can be achieved from THDP processing. This study focused on the relationship between hydrogen and Ti_3Al , and the effect of Ti_3Al on tensile performance. Consequently, some aspects of microstructure evolution were not fully explored. For instance, the triangular and indentation mark morphologies were observed in the THDP treated sample but not in its non-deformed (THP) counterpart. A texture evolution analysis at the transient stages of the THP and THDP treatments can provide more insights on the causes of the latter. This analysis can be recommended for a future follow up study since texture investigations were beyond the scope of this study.

From the aforementioned discussion chapters, this thesis concludes that;

1. The extent to which the hydrogenated microstructure reflects hydrogenation-disproportionation

Hydrogenation-disproportionation-desorption-recombination (HDDR) accounts for microstructure and tensile property evolution in hydrogen treated Ti-6Al-4V. The 20 at.% alloyed hydrogen precipitates low hydrogen bearing (Ti-H) and medium hydrogen bearing (Ti-H₂) hydrides. The hydride precipitates partition Al from its Ti-Al couple to form neighbouring Al rich clusters where the extent of Al enrichment stabilises Ti₃Al.

2. The extent to which the desorbed microstructure reflects microstructure recombination

Hydrogen desorption decomposes hydrides but it retains Ti₃Al precipitates in hydrogen treated microstructures after hydrogen escape. The degree of recombination improves with increasing dehydrogenation (or desorption) temperature from 675°C to 750°C.

2a) Microstructure recombination after 675°C dehydrogenation

The 675°C dehydrogenated microstructure is partially recombined. It has a high volume fraction of retained Al rich clusters (or Al rich nanobands in tempered martensite) which stabilise Ti₃Al precipitates. The retained Al rich clusters reduce ductility, this is because the retained Al rich clusters are the preferred pathway for crack propagation which indicates that they have a low resistance to crack propagation.

2b) Microstructure recombination after 750°C dehydrogenation

The 750°C dehydrogenated microstructure is significantly recombined. It has a significantly lower volume fraction of retained Al rich clusters (or Al rich nanobands in tempered martensite) which could stabilise Ti₃Al. However, the degree of Al enrichment in the HDH 750 treated sample was not sufficiently extensive to promote Ti₃Al precipitation. The 750°C dehydrogenated microstructure can have undissolved Ti₃Al precipitates because the 3 hour dehydrogenation at 750°C does not fully homogenise the Al concentration in hydride partitioned microstructures. This was confirmed in 750°C dehydrogenated martensite which reveals a low volume fraction of Ti₃Al precipitates after a 3 hour dehydrogenation at 750°C.

3. Effect of desorption (dehydrogenation) temperature on the microstructure and room temperature tensile performance

Temporary hydrogen treatment causes embrittling effects which remain in the microstructure after hydrogen is fully removed. The embrittling effects can be controlled by altering the dehydrogenation or desorption temperature. The desorption (or dehydrogenation) temperature determines the extent of microstructure recombination and in turn controls the tensile ductility of HDH and THP treated microstructures.

3 a) HDH treated and dehydrogenated at 675°C to 750°C

During a hydrogenation-dehydrogenation (HDH) treatment, the HDDR driven microstructure evolution refines the Widmanstätten microstructure by nucleating refined BCC grains within the coarse Widmanstätten lamellae. This refinement improves the strength of hydrogenated-dehydrogenated Ti-6Al-4V by up to 70 MPa (YS) and 100 MPa (UTS).

Dehydrogenation temperature and tensile ductility in HDH treated microstructures:

- Dehydrogenation temperatures below 750°C yield partially recombined microstructures which are prone to Ti_3Al embrittlement.
- The Ti_3Al embrittlement in HDH treated Ti-6Al-4V causes up to 75% ductility loss (at the 675°C dehydrogenation temperature).
- The 750°C dehydrogenation temperature causes extensive microstructure recombination which significantly dissolves Ti_3Al precipitates to extents that restore full ductility. However, 750°C dehydrogenated microstructures can have undissolved Ti_3Al precipitates (because the 3 hour dehydrogenation at 750°C does not fully homogenise the Al concentration in hydride partitioned microstructures).
- The HDH study shows that the volume fraction of Ti_3Al that may be present in 750°C dehydrogenated microstructures has an insignificant effect on ductility.

3 b) THP treated and dehydrogenated at 675°C

The combined effect of HDDR promoted grain refinement and martensite strengthening increases the strength of 675°C dehydrogenated martensite (THP 900-580-675) by up to 130 MPa (YS) and 142 MPa (UTS) but it also decreases tensile ductility by 60%. The contribution of hydrogen to the observed strength increase and ductility loss can be evaluated by deducting the tensile performance contributions that would otherwise occur in the absence of hydrogen, these are observed in the control 900-580-675 sample.

- If tempering non-hydrogenated Ti-6Al-4V which was quenched at 900°C (control 900-580-675) increases the strength by 90 MPa (YS) and 88 MPa (UTS) and also decreases the ductility by up to 30% from 10% to 8±1% elongation,
- then alloyed hydrogen contributes 40 MPa (YS), 54 MPa (UTS) to the strength increase and 30% to the ductility loss that is observed in 675°C dehydrogenated martensite.
- The contribution of hydrogen to the tensile performance of tempered martensite emanates from hydrogen promoted acicular martensite formation and hydrogen promoted Ti₃Al precipitation.
- Alloyed hydrogen promotes acicular martensite formation at a lower quenching temperature of 900°C. The acicular martensite microstructure has less ductility when compared to lamellar microstructures.
- Hydrogen tempering intensifies the ductility loss in acicular microstructures because it promotes Ti₃Al precipitation within 3 hours of aging at 580°C. Similarly tempering in the absence of hydrogen does not precipitate Ti₃Al.

3 c) THP treated and dehydrogenated at 750°C

Increasing the dehydrogenation temperature to 750°C coarsens martensite plates and dissolves a significant volume fraction of Ti₃Al precipitates. The plate coarsening softens martensite and causes a strength loss of 70 MPa (YS) and approximately 30 MPa (UTS).

- The combined effect of martensite softening and Ti₃Al dissolution at 750°C recovers 32% ductility.
- 12% of the recovered ductility is caused by martensite softening (because it is also observed in non-hydrogen tempered martensite). A net 20% of recovered ductility is caused by Ti₃Al dissolution at 750°C.

4. The influence of hydrogen tempering on martensite evolution in THP and THDP treated Ti-6Al-4V

Alloyed hydrogen prevents a complete parent BCC to HCP plate martensite transformation during quenching. It stabilises some of the BCC phase as a metastable phase at room temperature. The metastable BCC phase decomposes during subsequent aging to precipitate Ti-H and Ti-H₂ hydrides. The hydride precipitates nucleate in the interplate region (as fine hydrides), at plate boundaries (as linear hydrides) and within acicular plates (as nanobanded hydrides).

4 a) Effect of hydrogen on the degree of Al enrichment in tempered martensite plates

Elemental partitioning is a normal component of martensite decomposition. Alloyed hydrogen intensifies the extent of Al partitioning and enrichment to critical concentrations that stabilise Ti₃Al within 3 hours of tempering at 580°C. In the absence of alloyed hydrogen, Ti₃Al does not precipitate after tempering for 3 hours at 580°C.

An expected partitioning of Al towards HCP plates occurs during martensite tempering. Hydrides intensify the degree of partitioning and enrichment within tempered martensite plates in two ways:

- *Partitioning towards HCP plates:*
Linear hydride precipitates (observed in THDP treatment) nucleate at martensite plate boundaries and partition Al towards adjacent HCP plates. This enriches adjacent martensite plates with Al to critical concentrations that stabilise Ti₃Al precipitates.
- *Partitioning within HCP plates:*
Nanobanded hydrides (observed in THP and THDP treatments) nucleate within hydrogen tempered martensite plates. Nanobanded hydrides partition Al to neighbouring nanobands. This extensively enriches neighbouring nanobands with Al to extents that stabilise Ti₃Al precipitates.

5. The nanobanded morphology within tempered martensite plates

The nanobanded morphology is a typical hydride morphology that occurs when hydrides configure to a nucleation interface. It is not observed in non-hydrogen tempered martensite because the latter has no hydride precipitates. Hydrides configure to the nanobanded morphology after nucleating at nanosized shear bands within martensite plates. The nanosized shear bands are a lattice invariant deformation which occurs within martensite plates to accommodate Bain strain.

- The nanobands maintain the same crystallographic orientation as their parent acicular plate which indicates a coherent epitaxial growth of hydride precipitates within the parent HCP plate.
- The nanoband interface is coherent when viewed after inadvertent hydrogen escape because hydrides decompose to V rich alpha after room temperature hydrogen escape. The interface remains coherent because it borders HCP alpha crystals that are at the same crystallographic orientation.
- Hydrides decompose to V rich BCC when hydrogen tempered martensite is dehydrogenated at (675°C or 750°C). The BCC phase nucleates at the V rich nanoband.

6. The configuration of tempered martensite plates in THDP treated Ti-6Al-4V

Self-accommodation presents an indelible influence on the degree of morphology refinement that is achieved from THDP processing. This is because they influence the HCP variants that nucleate during the quenched, aged and dehydrogenated stages of the THDP treatment.

- Self-accommodation groups HCP variants to the 2 or 3 variant cluster morphologies to minimise strain.
- Consequently, selected HCP variants nucleate during the quenched, aged and dehydrogenated stages of the THDP treatment. The nucleated variants are grouped to 2 or 3 variant cluster morphologies.
- Consequently the submicron grained microstructure is configured to 2 or 3 variant cluster morphologies known as the indentation mark or triangular morphologies.

7. Elements of hydrogenation-disproportionation

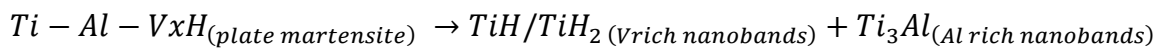
7a) Hydrogenated Ti-6Al-4V

The hydrogenated microstructure has elements of a hydrogenation-disproportionation reaction. Hydrogenation transformed lamellae alpha into distinct Al rich and V rich regions which ultimately stabilised Ti_3Al precipitates and beta grains. The hydrogenation-disproportionation half reaction for hydrogenated Ti-6Al-4V can be described by:



7b) Hydrogen tempered martensite

Hydrogen tempered martensite has elements of a hydrogenation-disproportionation reaction. Hydrogen tempering transformed martensite plates into distinct Al rich and V nanobands which ultimately stabilised Ti_3Al precipitates and beta grains. The hydrogenation-disproportionation half reaction for tempered martensite plates can be described by:



Similarly, hydrogen tempering transformed metastable beta into equilibrium alpha plus Al rich and V rich regions which ultimately stabilised Ti_3Al precipitates and beta phase respectively. The hydrogenation-disproportionation half reaction for hydrogen tempered metastable beta can be described by:



7c) Un-observed aspects of hydrogenation-disproportionation

Some of the proposed elements of hydrogenation-disproportionation were not observed in hydrogenated Ti-6Al-4V and hydrogen tempered martensite. For instance, literature proposes that hydrides reject vanadium during hydrogenation-disproportionation. However, this work observed that hydride precipitates are rich in vanadium and this observation was consistent in hydrogenated Ti-6Al-4V and hydrogen tempered martensite. This indicates that the distinct V rich regions do not originate from vanadium that was rejected from hydride precipitates but instead they originate from V rich hydride precipitates.

It can be concluded that the observed elements of hydrogenation-disproportionation support the hypothesis of the study which states that; hydrogenation-disproportionation accounts for the evolution of grain refinement and the promotion of Ti_3Al formation in hydrogen treated Ti-6Al-4V. However, the unexpected but observed enrichment of hydrides with vanadium reveals that refined beta grains nucleate from decomposing hydride precipitates, and not V rich regions that formed as a consequence of hydrides rejecting vanadium.

8. Additional conclusions: Vacuum exposure and dehydrogenation

8a) Room temperature vacuum exposure

Room temperature vacuum exposure inadvertently dehydrogenates electron transparent samples and this decomposes hydride precipitates to V rich alpha. The room temperature hydride decomposition has insufficient diffusion kinetics to promote Al and V diffusion. Consequently, it landmarks prior hydride regions as V rich alpha and it also retains the Al rich clusters that are caused by hydride induced partitioning. Therefore the effect of hydrogen on the microstructure can successfully be traced from hydride landmarks after inadvertent hydride decomposition.

8b) Elevated temperature vacuum exposure

Elevated temperature dehydrogenation of 12mm diameter and 100mm length tensile rods could be successfully traced by monitoring vacuum levels:

- Hydrogen escapes tensile rods after dehydrogenating above the hydrogen escape window which this is at temperatures above 410°C.
- The hydrogen escape depletes the vacuum from 10^{-5} mbar to 10^{-1} mbar. The rate of hydrogen escape peaks at approximately 630°C (150 minutes of experiment time). It gradually decreases thereafter and this consequently improves the vacuum.
- Significant hydrogen escape is achieved during 675°C dehydrogenation. There is a possibility that 675°C dehydrogenation could retain an infinitesimal degree of dissolved hydrogen in the sample. This infinitesimal concentration of retained hydrogen would not be sufficient to stabilise hydride phase nor embrittle the sample. In comparison, full hydrogen escape is achieved in 750°C dehydrogenated samples.

9. TECHNOLOGICAL IMPLICATIONS OF THE STUDY

Industry prefers wrought Ti-6Al-4V because it offers an attractive combination of mechanical properties. However, the manufacturing of Ti-6Al-4V components which involves machining from wrought Ti-6Al-4V stock has high production costs. Casting is an alternative manufacturing route which produces near-net shape Ti-6Al-4V components. These require minimal machining and consequently limit production costs. However, as-cast Ti-6Al-4V components do not have the best strength and ductility properties. This is because their as-cast Ti-6Al-4V microstructure has coarse grain sizes and a Widmanstätten morphology.

This study shows that temporary hydrogen treatment (THT) can significantly refine the coarse grain size and the Widmanstätten morphology of cast Ti-6Al-4V. In addition, it shows that the strength of cast Ti-6Al-4V can be consequently improved to extents that are comparable to wrought Ti-6Al-4V (provided there are minimal porosity defects). The ASTM F1472 standard stipulates the required strength and ductility for wrought Ti-6Al-4V. This study successfully optimised the performance of simulated cast Ti-6Al-4V to meet the ASTM F1472 requirements using HDH treatment.

The findings of this study open a window of opportunity for manufacturing Ti-6Al-4V components. Essentially, a cost competitive edge can be realised by manufacturing Ti-6Al-4V components using the cost effective casting route. The performance of cast Ti-6Al-4V components can be subsequently optimised to meet industry specifications using temporary hydrogen treatment.

However, a precise heat treatment protocol must be followed when optimising the performance of cast Ti-6Al-4V material using temporary hydrogen treatment. Dehydrogenation must be performed at temperatures above 750°C to prevent Ti_3Al embrittlement. This is mandatory for all hydrogen treated Ti-6Al-4V components that will be used for room temperature applications.

10. FUTURE WORK

10 a) Evaluating the tensile performance of THDP treated samples

The submicron grained microstructure attained from the THDP 675 treatment promises extensive strength improvement. However, Ti_3Al precipitates will deteriorate the tensile performance of the THDP 675 microstructure. This study has shown that increasing the dehydrogenation temperature to 750°C significantly reduces the volume fraction of Ti_3Al to extents that eliminate Ti_3Al embrittlement. However, this may also reduce the strength of THDP treated microstructures because of combined effects from martensite softening and grain coarsening.

Future work in the THDP study should upscale the deformation process to levels that allow ASTM compliant tensile samples to be extracted from the deformed material. The ASTM compliant tensile samples should be used to evaluate the tensile performance of THDP treated microstructures that were dehydrogenated at 675°C and 750°C . In addition, future work can evaluate the effect of dehydrogenating for shorter times at temperatures above 750°C on the tensile performance of THDP treated microstructures.

10 b) Evaluating the effect of deformation on texture evolution in hydrogen tempered martensite

The THP and THDP treatments have a similar heat treatment protocol, except that THDP incorporates a deformation step before martensite tempering. The triangular and indentation mark morphologies are more prominently observed in the THDP treated sample which incorporates a deformation step. Future work could explore the reasons behind the latter by investigating the effect of deformation and hydrogen tempering on texture evolution at the transient stages of the THP and THDP treatments.

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APPENDIX A: CALCULATING ABSORBED HYDROGEN FROM MASS GAIN (WORKED EXAMPLE)

Hydrogenated sample mass (g) - m_1	0.99
(-) Initial sample mass (g) - m_0	0.98
Mass of absorbed hydrogen (g) - m_H	0.01

Composition (90%Ti - 6%Al - 4%V - xH)	Units	0.9 Ti	0.06 Al	0.04 V	xH	Σ of rows
Molecular mass (mr)	g/mol	47.86	26.98	50.94	1	-
Calculation of mass of elements in (Ti-6Al-4V-xH)	g	$0.9 \times m_0$	$0.06 \times m_0$	$0.04 \times m_0$	m_H	-
Row A = Mass of elements in Ti-6Al-4V-xH	g	0.88	0.06	0.04	0.01	0.99
Row B = $((\text{row A} / \Sigma \text{ row A}) \times 100)$	wt.%	89.09	5.94	3.96	1.01	100
Row C = $(\text{row B} / \text{mr})$	-	1.86	0.22	0.08	1	3.16
Row D = $((\text{row C}) / (\Sigma \text{ of row C})) \times 100$	at.%	58.88	6.96	2.46	31.70	100