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Grain Structure Control of Titanium Alloys during Wire + Arc Additive
Manufacturing

School of Aerospace, Transport and Manufacturing
Welding Engineering and Laser Process Centre

PhD

Academic Year: 2019 - 2023

Supervisor: Prof. Stewart Williams
Associate Supervisor: Dr. Jialuo Ding
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This thesis is submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy

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Abstract

Prior- β grain structure control of titanium alloys during Wire + Arc Additive Manufacturing (WAAM) is reliant on post-processing following deposition. Multiple methods are typically employed including cold working, melt pool agitation, inoculation and constitutional additions, all of which have distinct limitations. This research has demonstrated prior- β grain structure control in the as-deposited condition whilst utilising a stable deposition process. Prior- β grain structure control of Ti-6Al-4V was achieved through the reduction of the specific energy density of deposited material (SED). As SED decreased, the thermal gradient and potential for constitutional supercooling increased. A linear thermal gradient approximation was calculated via pyrometry to record the melt pool temperature. The SED was controlled via the wire feed speed and fixed energy input. It was determined that SED did not affect the peak melt pool temperature. Instead, arc shading was responsible for the cooling of the melt pool. Electron back-scattered diffraction (EBSD) analysis demonstrated a refinement of the prior- β grain morphology and weakening of texture. Analysis of the prior- β grain boundary misorientations demonstrated that as SED reduced, the misorientations had a propensity to the Mackenzie distribution. However, distinct peaks of $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ misorientations were observed and the tilting of grains to the deposition direction. The SED hypothesis was tested using various process parameters and additional titanium alloys, Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr, which had an increased potential for constitutional supercooling. It was determined that SED was not the primary mechanism behind prior- β grain refinement. Instead, dendrite twinning in the $\{332\}_\beta \langle 113 \rangle_\beta$ and $\{112\}_\beta \langle 111 \rangle_\beta$ during solidification characterised by $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ misorientations respectively, as melt pool curvature, measured by the length/depth ratio proxy, increased. The single energy source deposition was limited by the reliance of melt pool shape on the SED. Therefore, the applicability of a scanning laser and arc multi energy source (MES) system was investigated for the deposition of Ti-6Al-4V. It was demonstrated via optical microscopy that the bead width, height and melt pool length could be independently controlled from the SED. Using the MES system various melt pool length/depth ratios were deposited whilst maintaining an equivalent SED. This confirmed the melt pool shape as controlling factor of the prior- β grain structure morphology via EBSD analysis.

Keywords: Plasma arc welding, direct energy deposition, columnar-to-equiaxed transition, laser welding, hybrid additive manufacturing, melt pool shape control, dendrite twinning, specific energy density.

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List of Publications

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Nomenclature

A_sArea of beam	P_sPower loss through substrate
A_oAmplitude of oscillation	P_ePower loss through environment
B_dBeam diameter	ρDensity
C_LLocal composition	q_pPower density
dWire diameter	rRadius
F_sScan frequency	$S(\theta)$Shape factor
G_sFree energy of solid	T_LLiquidus temperature
G_LFree energy of liquid	T_GTemperature gradient
HBead height	τ_iInteraction time
IArc current	VArc voltage
kPartition coefficient	v_sScan velocity
η_AArc efficiency	v_aMES travel speed
n_iNumber of interactions	WBead width
σ_{BS}Surface energy at boundary-solid interface	w_sScan width
σ_{SL}Surface energy at solid-liquid interface	γSurface energy at solid-liquid interface
θWetting angle	
PLaser power	
P_tPower transferred to workpiece	
P_aTotal power applied	
P_mPower to generate melt pool	

Abbreviations

Alternating current(AC)	Direct energy deposition.....(DED)
Additive manufacturing(AM)	Direct current electrode
Aluminium(Al)	negative(DCEN)
Alpha phase.....(α)	Direct current electrode
Beta phase.....(β)	positive(DCEP)
Body centred cubic(BCC)	Electron beam melting(EBM)
Burger's orientation relationship..(BOR)	Electron beam freeform
Buy-to-fly(BTF)	fabrication(EBF ³)
Build direction(BD)	Electron back-scattered
Back-scattered electron.....(BSE)	diffraction(EBSD)
Carbon dioxide(CO ₂)	Energy-dispersive X-ray(X-EDS)
Computer aided design(CAD)	Effective wall width(EWW)
Computer numerical control.....(CNC)	Heat affected zone(HAZ)
Cumulative energy demand(CED)	Hexagonal close packed(HCP)
Columnar-to-equiaxed	Heat input(HI)
transition(CET)	Inverse pole figure(IPF)
Chromium..... (Cr)	Inter-lamellar spacing(ILS)
Commercially pure titanium(CPTi)	Low angle grain boundaries(LAGB)
Contact tip work distance.....(CTWD)	Laser metal deposition(LMD)
Continuous alpha grain	Length/depth ratio(L/D)
boundary(α_{GB})	Metal additive manufacturing...(MAM)
Direct current..... (DC)	Manufacturing time(Mfg.)

Multi-energy source	(MES)	Wire + arc additive	
Metal inert gas	(MIG)	manufacturing.....	(WAAM)
Molybdenum	(Mo)	Welding Engineering and Laser	
Neodymium: ytterbium-aluminium-		Processing Centre.....	(WELPC)
garnet	(ND:YAG)	Working direction.....	(WD)
Plasma transferred arc.....	(PTA)	Wire + laser additive	
Selective laser melting	(SLM)	manufacturing.....	(WLAM)
Selective laser sintering	(SLS)	Wire feed speed/travel speed	
Secondary electron		ratio	(WFS/TS)
microscopy	(SEM)	Wire feed speed	(WFS)
Silicon	(Si)	Yttrium	(Y)
Specific energy		Zirconium	(Zr)
density.....	(SED)		
Solidification rate	(R)		
Titanium nitride	(TiN)		
Tin	(Sn)		
Tungsten inert gas	(TIG)		
Travel speed	(TS)		
Transfer mode	(TM)		
Transverse direction	(TD)		
Thermal gradient	(G)		
Ultimate tensile strength	(UTS)		
Vanadium	(V)		

1. Introduction

1.1 Research Background

Additive manufacturing (AM), more commonly referred to as ‘3D-Printing’ or ‘rapid prototyping’, is increasingly seen to be the future manufacturing option of choice for a number of industries. It is based upon the creation of homogenous net-shape components, or near-net shape preforms in a successive layer-by-layer deposition process. Whilst many variants of AM exist, metal additive manufacturing (MAM) has caught the attention of large-scale industrial manufacturers. MAM is an emerging process that is swiftly becoming a viable commercial option to rival traditional manufacturing technologies such as machining, casting and forging [1].

In the case of MAM, build quality is based upon the type of deposition method used and deposition rate [2]. Generally, the creation of near-net shape components or preforms [3] requiring some form of post-processing is not uncommon [4]. Corresponding to all AM processes, the MAM process can be simplified into several distinct stages: the generation of a computer-aided design (CAD) model; model slicing (whereby discrete layers are generated; tool path planning; deposition of component and an optional step to machine and/or heat treat the deposit [5].

In comparison to more well-established traditional manufacturing methods, MAM is evolving at a faster rate. Whilst not in its infancy, work is still required before adoption of MAM into the mainstream, particularly around the qualification of deposited components [6]. The earliest recorded account of a MAM process was in 1920, when Ralph Baker submitted a patent to utilise arc welding to “...*produce receptacles or containers of ornamental and useful shapes.*” [7] as illustrated in Figure 1-1. However, it would not be until almost 100 years later that the technology would flourish, with multiple variants of MAM technologies available.

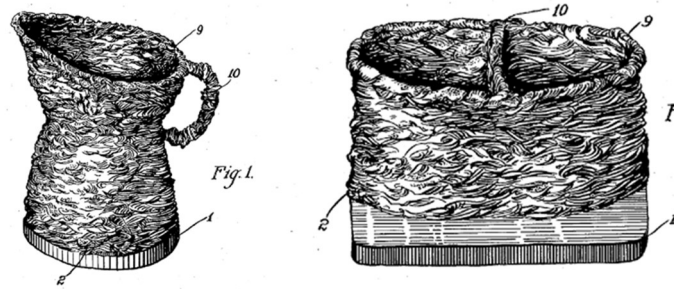


Figure 1-1: Excerpt illustrations of the first patented metal additive manufacturing components, using arc welding [7].

The AM philosophy boasts several advantages over its traditional manufacturing counterparts:

- AM provides a significant reduction in total machining costs compared to subtractive manufacturing. As near-net shape components are deposited, they represent the final geometry as closely as possible, requiring minimal refining. A common measure within the manufacturing industry is the metallic yield (a measure of how much material is required to manufacture a component versus how much is retained in the final product), in the aerospace industry this is referred to as the buy-to-fly (BTF) ratio. Typical BTF can be upwards of 20:1 for subtractive manufacturing techniques. Whilst the metallic yields of casting processes can be as low as 4:1 – 1.2:1 for investment (or even general) casting but is dependent on process configuration [8,9], AM processes typically offer consistent BTF ratios as low as < 1.5:1 (dependent on AM process and lead time) [10].
- The use of AM transforms the ability of a designer to develop complex structures as they are no longer restricted by machining or tooling constraints. This allows for the development of new geometries, including complex internal features that would otherwise be impossible to create as a single component. Additionally, the requirement for sub-assemblies may be reduced or eliminated and homogeneous components built through the consolidation of assemblies. Such a consolidation approach is highly beneficial and is being considered by other industries including the automotive sector where Tesla has introduced ‘gigacasting’, aiming to reduce the number of components and per unit manufacturing cost through casting a singular chassis structure rather than relying on the joining of multiple components. Whilst this approach has a flat cost structure compared to traditional joining assembly lines,

other benefits are achieved such as total weight reduction and improved manufacturing productivity [11].

- The lead times of additively manufactured parts are significantly shorter than traditional techniques, hence the moniker ‘rapid prototyping’, and remove the need for costly tooling. This allows small and medium batch components to be produced with little economic cost, allowing bespoke components to be generated, requiring only a small tweak in CAD geometry and path planning.
- The implementation of AM can shorten the research and development cycle as the generation of prototypes and optimisation cycles can be carried out more effectively, catering for greater design freedom, scope and optimisation.

Given the undeniable benefits of the aforementioned advantages begs the question as to why AM has not yet been fully adopted into mainstream manufacturing. Process specific disadvantages do occur and in general AM is still considered to require further process qualification, as each currently deposited component is regarded as a bespoke component [6]. The qualification of AM components is being heavily scrutinised by industry. Companies such as WAAM3D Ltd, a spinoff of the Cranfield University Welding Engineering and Laser Processing Centre, are considering this aspect alongside academia, with a particular emphasis on in-line defect monitoring [12].

A particular industry keen to realise the deployment of MAM technologies is aerospace, where there is an established demand for reducing the BTF ratio. In part this is due to the transition of using titanium components from aluminium, as a result of the increased number of composite materials and titanium’s electro-compatibility [10,13], but also that titanium is an expensive material to extract. Titanium is not found as a pure element, it exists in the form of titanium oxide which is required to undergo a reduction process. Coined the Kroll process, titanium oxide is converted into titanium chloride and then reduced with magnesium or sodium, before being cast into ingots [14]. In addition to this refining process, the machining cost of titanium is also expensive. Inherent material properties make it prone to chipping during machining and its low thermal conductivity generates high thermal stresses on the required tooling [15], making it an ideal candidate for additive manufacturing.

For the creation of medium to large scale additively manufactured components required in the aerospace industry, Wire + Arc Additive Manufacturing (WAAM) is ideally placed. A basic WAAM system utilises standard ‘off the shelf’ welding equipment, comprised of: a welding power source, an automated wire feed system and manipulator (robotic or computer numerical control (CNC) gantries [16]), with options to employ numerous process monitoring technologies. This permits the deployment of a WAAM system for a low capital investment cost, with readily available feedstock materials in the form of welding wire [10]. Similar to other AM processes, WAAM generates components through the successive deposition of weld layers that remelt the previously deposited layers, to form homogenous components of single or even multiple alloys [17]. An example of the versatility of WAAM can be observed in Figure 1-2, with various components, of various sizes and alloys shown. For complex geometries, robotic systems appear to give greater utility than XYZ CNC gantry systems, with more axes available for deposition [16].



Figure 1-2: Examples of various complexity parts built using wire + arc additive manufacturing from steel and titanium [35,36].

Cranfield University coined the name WAAM [18] and first began research into the technology in the 1990’s undertaking a shaped metal deposition project for Rolls Royce. Subsequently, the University has been pivotal in the research and development of this technology and has received a number of project grants, working alongside industry to explore the technology and mature its technology readiness level. Notable research programmes include:

- The Ready to Use Additive Manufacturing project (131), funded by the Innovative Manufacturing Research Centre and Engineering and Physical Sciences Research

Council (EP/E001874/1), aimed at integrating multiple axes to both deposit and machine WAAM components on a single machine.

- The Cranfield University led WAAMMat technology development programme comprising a series of research projects and activities in collaboration with over 10 academic partners and 30 industry partners, aimed at maturing WAAM's technology readiness level to 6.
- The EPSRC New Wire + Arc Additive Manufacturing programme (EP/R027218/1), aimed at transforming large-scale MAM and providing new high build-rate processes at low cost with tailored microstructure and mechanical properties.
- The current EPSRC funded Sustainable Additive Manufacturing (EP/W01906X/1) project, aimed at reusing swarf material with an innovative skin and core deposition approach to immensely reduce cost and carbon footprint.

The culmination of WAAM research undertaken at Cranfield University has led to the publication of more than 275 research papers, 40 successful PhD projects and 100 MSc projects. In 2018 WAAM3D Ltd. was formed as a spin-out from Cranfield University and has subsequently developed into a multi-million-pound company, employing over 30 staff [19], providing a WAAM turn-key solution, including the raw material, WAAM cell, process development, services and support.

As the WAAM process has matured, so has the ability to generate increasing levels of component complexity and size. The initial goal of WAAM was to deposit large scale structures with high geometrical fidelity. Initial studies conducted highlighted the importance of controlling thermal compensation, i.e. changes in geometry, for example at intersections which alter the local heat extraction rate and thus bead geometry. As demonstrated in Figure 1-3 a 1.2 m titanium wing spar, developed in collaboration with BAE Systems, demonstrated a continuous undulation along its length, which initially is hidden dependent on viewing perspective.

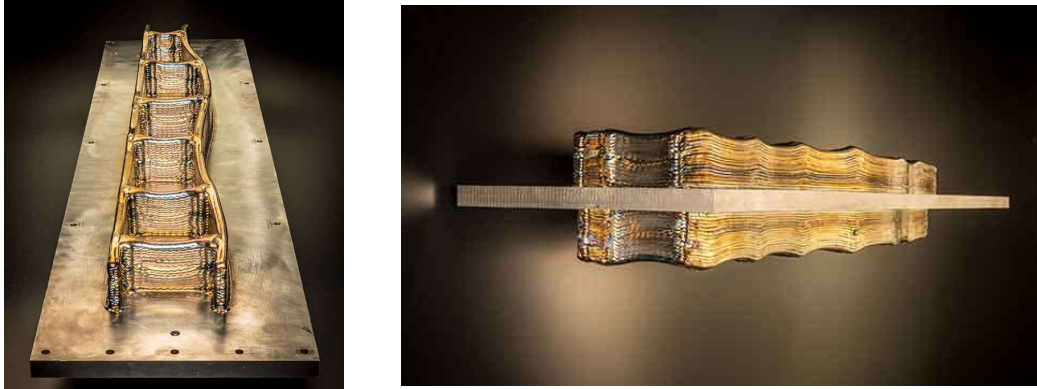


Figure 1-3: Ti-6Al-4V wing spar deposited with WAAM in collaboration with BAE Systems, measuring 1.2 m in length. Note on along the length of the deposited component an undulation, highlighting the need for thermal mass compensation at intersections. Reproduced from [38].

More complex components have since been developed including a landing gear rib for Bombardier, produced both in mild steel and Ti-6Al-4V, with a 0.6 m x 0.6 m footprint as may be observed in Figure 1-4. It may be noted that layer height is maintained across the deposit, where several features are deposited including intersections and linear and angular strengthening ribs. In addition, the ability to deposit symmetrically on the substrate minimises residual stress and distortion, as may be observed in the evenness of the substrate.

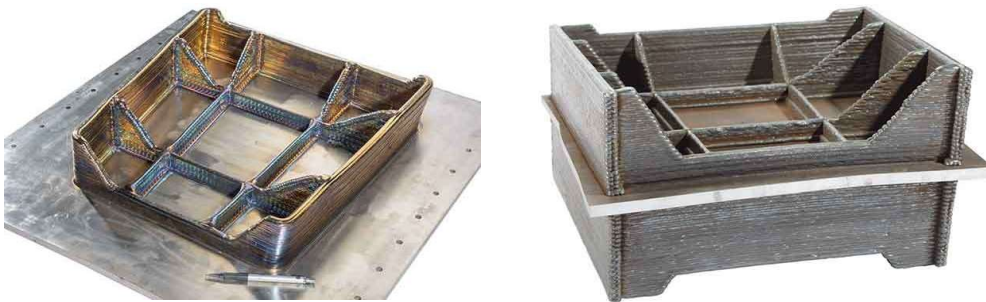


Figure 1-4: (L) Bombardier outboard landing gear rib deposited in Ti-6Al-4V (R) Identical Bombardier outboard landing gear rib deposited in mild steel. Reproduced from [39].

In addition, Cranfield University deposited components have been tested to technical requirements and specifications. An example of a 1 m high Ti-6Al-4V pressure vessel deposited in collaboration with Thales Alenia Space may be observed in Figure 1-5. This component was stress-relieved, laser scanned, machined and inspected via ultrasonics and computer tomography, demonstrating full density and no defects. The deposition of this pressure vessel led to an overall material savings of 80% compared to its normal manufacturing process, with a cost saving of 40% and lead time reduction of 65%, whilst simultaneously consolidating two integrated components into a single part. A similar pressure vessel application may be observed in Figure 1-6, where a satellite propellant

tank was produced by Cranfield University in collaboration with Airbus Space. WAAM production of this component led to a 50% cost reduction, reduction in lead times and exceeded the mechanical performance of the conventionally manufactured component. An additional benefit for these types of components is the ability to manufacture a bespoke size for each flight.

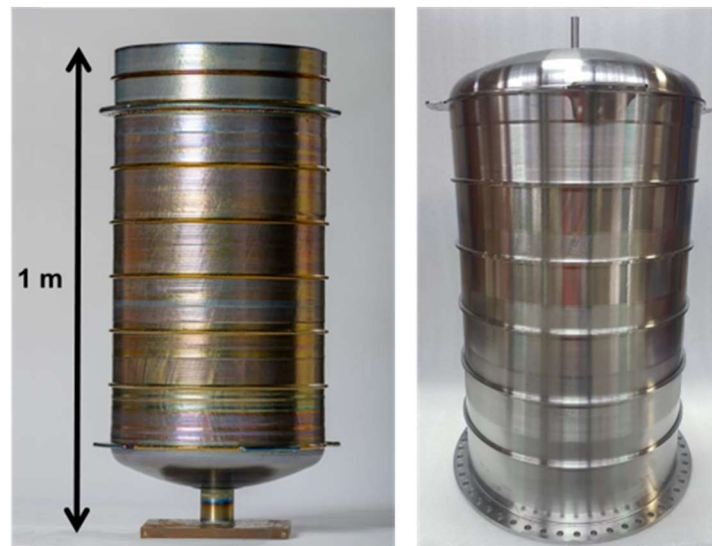


Figure 1-5: (L) Deposited Ti-6Al-4V pressure vessel in collaboration with Thales Alenia Space measuring 1 m in height (R) The WAAM deposited pressure vessel post-machining. Reproduced from [40].

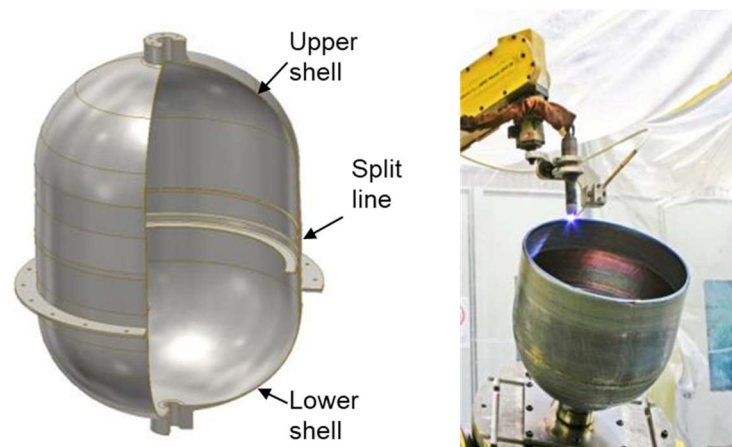


Figure 1-6: (L) Computer-aided-design 3D render of satellite propellant tank to be deposited. (R) Partway deposition of Ti-6Al-4V satellite propellant tank for Airbus Space. Images provided by Cranfield University.

In addition to cruciform and cylindrical deposited components, WAAM is capable of much more complex deposition geometries for more specialised applications. Such niche applications are highly suitable for additive manufacturing rather than high quantity batch manufacturing, which is better suited to conventional manufacturing processes such as

casting. Figure 1-7 shows the rear engine mount for a Eurofighter Typhoon combat aircraft, deposited with Ti-6Al-4V to support dual Eurojet EJ200 engines capable of producing 60 kN of thrust. Whilst the mechanical properties of this part have not been disclosed, it has been disseminated that the fatigue properties of this part are equal to or better than the current conventional forgings used to produce this part. This particular component deposited at Cranfield University in collaboration with BAE Systems is the world's largest 3D printed titanium component at $\sim 2\text{ m} \times 1.5\text{ m}$. A significant aspect for the generation of this part was the reduction in lead time from ~ 100 weeks to ~ 100 days.

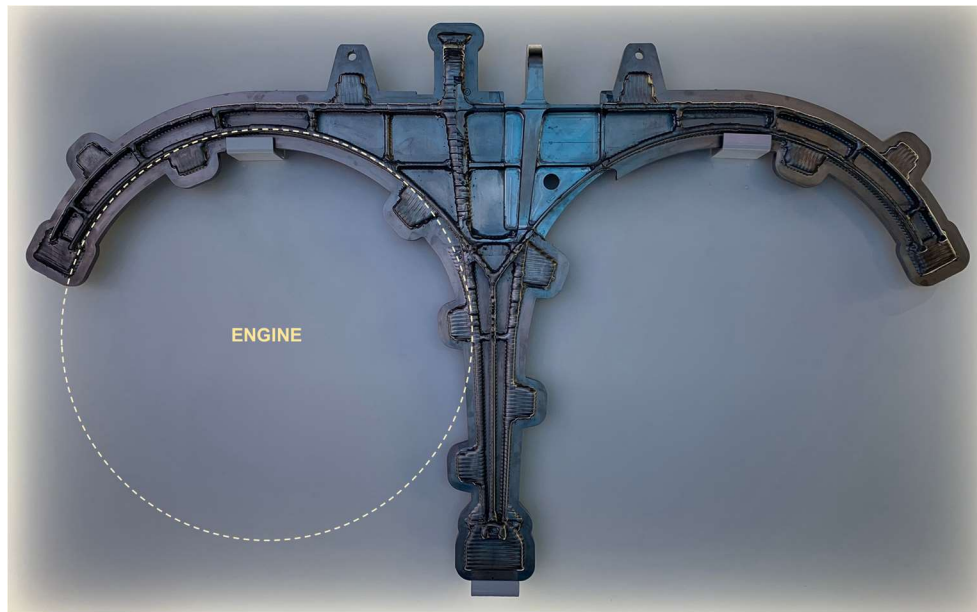


Figure 1-7: As-deposited Ti-6Al-4V Eurofighter Typhoon rear engine mount deposited by Cranfield University in collaboration with BAE Systems. Note: At the time of writing this remains the largest 3D printed titanium deposition in the world.

Whilst the development of WAAM at Cranfield University has largely been influenced by the aerospace industry, it should be noted that other industries are interested in the commercialisation and application of WAAM, including mining, oil and gas and construction etc. It is evident that accurate geometrical accuracy can be achieved in WAAM and that the generation of complex geometries and consolidation of sub-assemblies can be achieved. However, before adoption into the mainstream, there is a clear requirement for scientific and standardised in-situ process and defect monitoring to ensure the correct geometry, microstructure and mechanical properties at the point of deposition [20,21]. Subsequently this will enable the qualification of components and wider application within industry [18].

A major focus of research into titanium alloy deposition using WAAM has focused on the development of Ti-6Al-4V. This particular titanium alloy accommodates over 50% of the titanium produced globally [22], due to its high specific strength, corrosion response and electrochemical compatibility with composite materials [13]. However, several distinct challenges exist in relation to the as-deposited microstructure and mechanical properties deposited by WAAM. The partial remelting of previously deposited layers, combined with a high thermal gradient, leads to epitaxial prior- β grain growth during solidification [23]. This manifests as large columnar grains visible to the naked eye, generally extending from the bottom to the top of a component as may be observed in Figure 1-8. The result is an anisotropic mechanical response as a consequence of differing levels of grain boundary α present in differing loading directions [23,24].

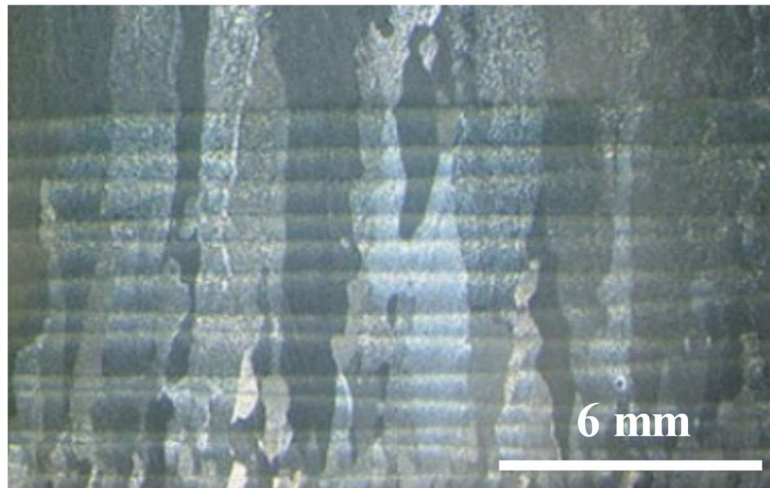


Figure 1-8: Example of prior- β columnar grain structure visible in Ti-6Al-4V when deposited using WAAM [37].

Investigation of the literature has identified that a large proportion of WAAM research has focused predominantly on the increase in productivity and deposition of net-shape components, rather than the ability to control prior- β grain structure during deposition, which is considered inherently problematic from a metallurgical standpoint [25]. The ability to deposit an equiaxed prior- β grain structure without intervention has yet to be routinely achieved in WAAM for Ti-6Al-4V, but is imperative for isotropic material properties. Yet, as the above focus has been achieved, the control of grain structure in the as-deposited condition is now becoming of increasing interest, with its ability to tailor mechanical properties locally and the underlying mechanism of refinement of interest to this research's industrial partner, BAE Systems Ltd.

Achieving the columnar-to-equiaxed transition (CET) is extremely difficult in Ti-6Al-4V in the as-deposited condition due to the insignificant amount of constitutional supercooling that exists, preventing nucleation ahead of the solidification front [25–27]. This allows only highly textured $\langle 100 \rangle_\beta$ prior- β grains to manifest by epitaxial growth [23,27,28]. Consequently, mechanical processing methods such as machine hammer peening [29,30] and rolling [31] have been introduced to force the potential for β grain recrystallisation. However, whilst successful, such processes demonstrate prior- β grain size variation between the inner and outer surface as well as an additional process step, requiring further economical and intellectual cost, negating some benefit of the WAAM process.

Others have focussed on the addition of growth restriction or inoculation of nucleant particles to the melt pool during deposition. These are typically slowly diffusing elements such as molybdenum [25] which increase the constitutional supercooling, or growth restricting particles such as boron and yttrium [32,33] which act as nucleation sites ahead of the solidification front to promote competitive dendritic growth. Unfortunately, the addition of these elements can lead to the formation of ‘dirty’ alloys whereby undesirable phases and intermetallic compounds can occur [32,34] and the mechanical property response is altered. As such, few studies have demonstrated success in achieving CET in the ‘clean’, as-deposited condition and do not provide a robust technique for doing so, thus, highlighting a research gap.

1.2 Aims and Objectives

1.2.1 Aim

The aim of this research was to investigate the columnar-to-equiaxed transition of the prior- β grain structure during the deposition of a wire + arc additively manufactured titanium alloy in the as-deposited condition, whilst concurrently identifying the mechanism of refinement.

1.2.2 Objectives

To achieve the aim of this study, the following objectives were set:

- 1 To consider variable performance parameter effects during Wire + Arc Additive Manufacturing and their impacts on the prior- β grain structure and mechanical properties.
- 2 To investigate methods to control the columnar-to-equiaxed transition of selected titanium alloys during Wire + Arc Additive Manufacturing via the control of thermal gradient and growth velocity and their impact on the prior- β grain structure.
- 3 To characterise the microstructure of the deposited titanium alloys with consideration of thermal profile during the Wire + Arc Additive Manufacturing process.
- 4 To investigate methods to independently control bead geometry and processing parameters during deposition.
- 5 To deposit structures with independent control over bead geometry and prior- β grain structure.

1.3 Methodological Approach

A deductive methodological approach has been utilised during this research, such that the strategies used to investigate the research objectives were generated based upon underlying theory of existing research. The objectives of the research were investigated experimentally, adopting a systematic and scientific method, through the controlled manipulation of selected variables and an instrumented response measured. Data collection and analysis followed an explanatory sequential research design, whereby quantitative data was emphasised and supported by qualitative data.

As the WAAM process holds commercial interest, all experiments were conducted in-situ i.e. in their normal operating environment to preserve real-world application. As expected, in some cases an abstracted approach was required, however, this was limited wherever possible. Each study was subjected to the construction of an experimental design, the purpose of which was to identify experimental variables, selection and calibration of instrumentation, and conduction of pilot studies to test the experimental design.

To ensure validity of the research, various methods of quality assurance were implemented: a sufficient level of induction and training of required apparatus for experimentation and analysis; generation of a data management plan and submission of ethical approval to Cranfield University and funding body standards; documentation of experimental procedures and methods; detailing an unbiased documentation of observations in the form of experimental logbooks (handwritten and digital); appropriate handling of samples and materials outlined within training and adherence to industrial standards (where possible) during testing and analysis.

For clarity, the methodological approach is demonstrated diagrammatically in Figure 1-9.

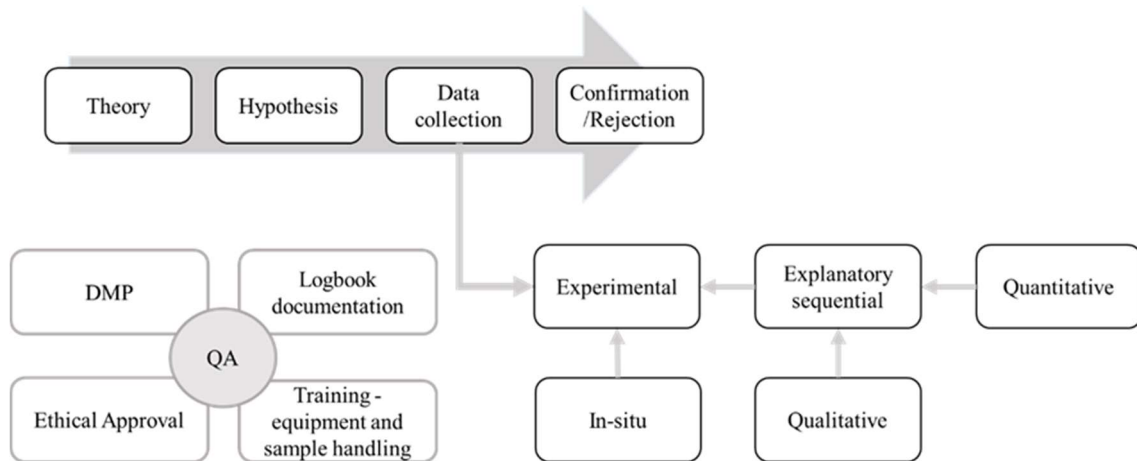


Figure 1-9: Methodological approach of the thesis.

1.4 Thesis Structure

The thesis is presented in accordance with the Cranfield University paper format thesis requirements. It is submitted as a collection of journal papers either under preparation, submitted or published in leading academic journals. As part of the formal submission criteria, there is no requirement for a standalone literature review, as each paper based technical chapter has considered the relevant literature as part of the paper submission. However, a short review of literature and theoretical framework is provided for context and to the benefit of the reader, as per requirement.

The thesis consists of 6 chapters:

Chapter 1: Provides an introduction to the research background, aims and objectives of the thesis, and methodological approach.

Chapter 2: Provides an introduction to metal additive manufacturing processes; a focus on Wire + Arc Additive Manufacturing; fundamentals of arc and laser deposition; fundamentals of titanium material characteristics and solidification theory; a focus on Ti-6Al-4V microstructure during Wire + Arc Additive Manufacturing; existing grain refinement techniques and their limitations and research gap. (Objective 1)

Chapter 3: The refinement of Ti-6Al-4V prior- β grain structure control in the as-deposited conditions via process control is demonstrated. The specific energy density of deposited material is considered as a controlling factor of prior- β grain structure morphology. However, it is indicated that the melt pool shape must also be taken into consideration. Electron back-scattered diffraction analysis demonstrated the columnar-to-equiaxed transition of prior- β grains for a stable deposition condition (Objectives 2 and 3).

Chapter 4: The effect of melt pool shape on prior- β grain structure morphology is considered to be a primary factor in grain structure control for Ti-6Al-4V. A new mechanism of prior- β grain structure refinement in the form of dendrite twinning during solidification is suggested. Electron back-scattered diffraction analysis determined that $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ dominated the grain boundary misorientations, corresponding to easily activated twinning systems in titanium alloys (Objectives 2 and 3).

Chapter 5: The applicability of a novel multi-energy source deposition process to Ti-6Al-4V is demonstrated to allow control of melt pool shape alongside independent control of bead width and height from thermal input. The specific point energy required to deposit with accurate control of melt pool shape is investigated and the process optimised for additive manufacturing of titanium. Using the multi-energy source system, the effect of melt pool shape on prior- β grain structure control is considered, isolating all process variables other than melt pool shape (Objectives 4 and 5).

Chapter 6: The culmination of all results is considered and final conclusions presented, considering the impact of the research and future work to be undertaken.

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2. Literature Review and Theoretical Framework

The following chapter will explore the literature surrounding Wire + Arc Additive Manufacturing (WAAM) with a focus on titanium alloys. Sufficient background will be presented to provide the theoretical framework which underpins the research. Therefore, this chapter will detail the relevant information with regards to classification of additive manufacturing processes; arc and laser welding processes; titanium alloy systems; solidification theory and an introduction to prior- β grain refinement mechanisms.

2.1 Classification of Additive Manufacturing Processes

Additive Manufacturing (AM) is an umbrella term that is used to describe several processes that rely on an energy source to fuse, melt, or solidify a powder, wire or resin feedstock, to form near-net shape components generated in successive layer-by-layer deposits. A plethora of materials are used in AM, including polymers, ceramics, composites and metals [1]. However, with the focus of this research being the deposition of titanium alloys, Metal Additive Manufacturing (MAM) will be discussed exclusively.

Several MAM processes exist and are classified by their energy source, feedstock form and feedstock delivery method [2]. Energy sources used in MAM may be either an electron beam, laser beam or electric arc. The feedstock form may be wire or powder. The feedstock delivery method is classified as powder-bed or directed energy deposition. Whilst various combinations exist, seven primary processes can be distinguished [3]: Electron Beam Melting (EBM); Electron Beam Freeform Fabrication (EBF³); Selective Laser Melting (SLM); Selective Laser Sintering (SLS); Laser Metal Deposition (LMD); Wire + Laser Additive Manufacturing (WLAM) and Wire + Arc Additive Manufacturing (WAAM). The use of a powder feedstock with an electric arc is generally avoided, due to the arc pressure preventing the powder feedstock entering the melt pool and/or the powder simply being blown away [4]. However, novel systems are being developed to incorporate powders with a wire feedstock, such as Wire-Powder-Arc Additive Manufacturing (WPA-AM) [5]. The primary MAM techniques are illustrated diagrammatically in Figure 2-1.

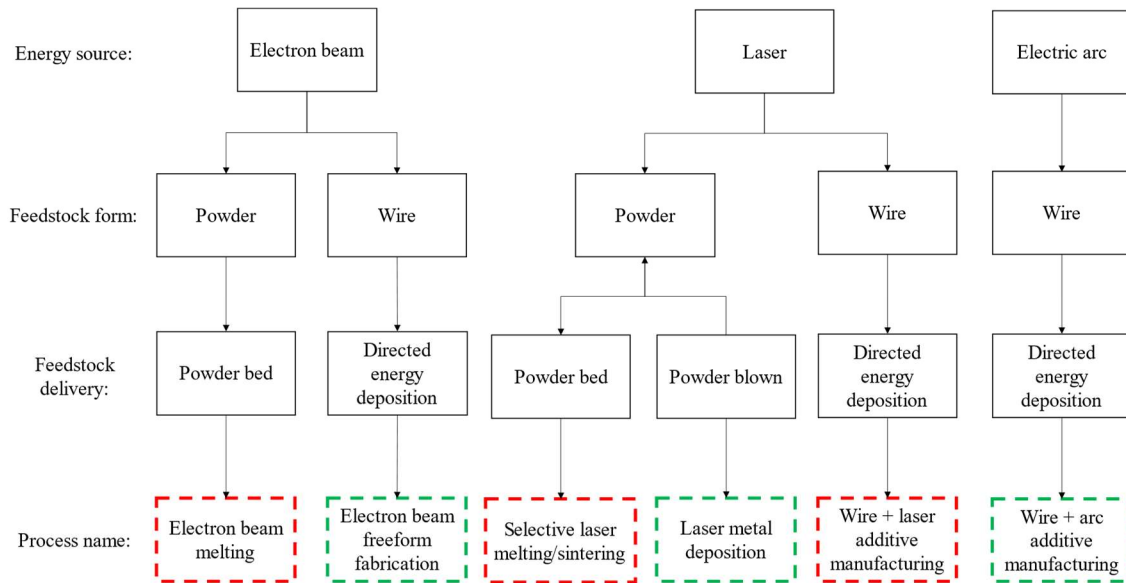


Figure 2-1: Classification of additive manufacturing processes, distinguished by energy source, feedstock form and delivery method. Adapted from [3].

The choice of MAM process is dependent on the application of the component to be deposited, each process has distinct advantages and disadvantages. Primarily, these are determined by the build time, resolution, potential defects, microstructure and mechanical properties.

2.1.1 Powder Metal Additive Manufacturing

Powder processes such as SLS, EBM and LMD, couple micro-scale powder (10 – 60 μm) feedstock with beam energy sources to concentrate vast amounts of energy over small areas, generating micro-scale melt pools [6]. This provides these processes with a means to deposit highly complex net-shape components with high resolution features and internal passages, which require little to no post-processing [2]. In the case of the medical industry for example, these advantages are highly desirable [7]. The availability of metal and alloy powders such as aluminium, titanium, copper, nickel, steels and high entropy alloys, make powder processes extremely versatile [8].

Powder feedstock delivery occurs in two formats, powder-bed or powder-blown. Powder-bed processes involve the moving of the heat source over a bed of powder to melt, in the case of SLM, or sinter (i.e. fuse the powder feedstock), in the case of SLS, before a new layer of fresh powder is distributed over the surface by a roller [9]. Powder blown processes use an inert gas carrier to supply powder feedstock directly to the melt pool and heat source path. This form of feedstock delivery is referred to as directed energy

deposition (DED) [9]. An illustration of powder-bed and powder-blown processes are illustrated in Figure 2-2.

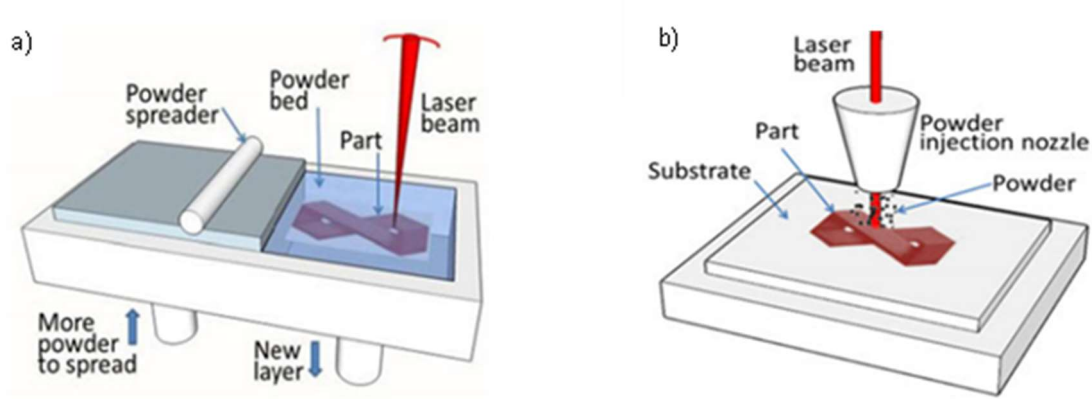


Figure 2-2: Illustration of powder AM processes a) powder-bed configuration b) powder blown configuration. Reproduced from [9].

The primary difference between the deposition of laser and electron beam processes, such as SLM and EBM, is the deposition environment. In laser beam processes, deposition is conducted within an inert atmosphere, whilst electron beam processes require a vacuum ($< 10^{-4}$ Pa) in order to operate to avoid electrons scattering as a result of collision with air molecules. In reality, the system is bled with helium gas to aid heat condition and component cooling, increasing the deposition atmospheric pressure to 10^{-2} Pa [6]. In electron beam processes, this essential lack of atmosphere leads to a reduction in the deposited component cooling rate, whilst, for laser beam processes the cooling rate is typically higher, due to convective cooling from the ambient atmosphere [10]. For certain materials such as Ti-6Al-4V, this leads to a difference in the transformation microstructure and thus mechanical properties [11,12]. Therefore, it is common to observe Ti-6Al-4V components with a lower yield strength and high ductility manufactured by EBM, than for an equivalent SLM Ti-6Al-4V deposit [10].

The primary benefit of powder and beam processes is the ability to manufacture components with a high resolution, i.e. net-shape [2], for example as may be observed in Figure 2-3, a Ti-6Al-4V Airbus A350 XWB cabin bracket manufactured using SLM [13]. However, the distinct disadvantage of powder processes is a low deposition rate, meaning comparatively large leads times relative to an arc-based process for comparable size components. Deposition rates for powder processes range from $9 - 120 \text{ g.min}^{-1}$ [14,15],

in contrast to electric arc and wire process with deposition rates that typically range from $1 - 4 \text{ kg}\cdot\text{hour}^{-1}$, and in some instances upwards of $10 \text{ kg}\cdot\text{hour}^{-1}$ [14].



Figure 2-3: Airbus A350 XWB cabin bracket manufactured by SLM in Ti-6Al-4V. Note the net shape of the component and complexity of multiple features. Reproduced from [13].

A further disadvantage of components manufactured using a powder feedstock is the prevalence of porosity within the final component, making manufacturing consistency difficult to achieve [16]. In powder processes, porosity is initiated by powder stacking vacancies that leave interstitial space between particles, i.e. gaps left between powder particles, which leads to the entrapment of gases during deposition [17]. During powder-blown processes, porosity is typically caused by partially molten particles adhering to the surface of melt pool and not fully melting [18]. Regardless of cause, porosity is severely detrimental to mechanical properties, acting as initiation sites for premature failure via cracking [19]. This prevents the use of powder generated MAM components from being used in structural applications [20].

Porosity can be reduced using hot isostatic pressing (HIP), which closes pores by compressing the material [21]. However, this method is not 100% effective and adds further process complexity and cost during the deposition process, reducing the commercial scalability of powder processes for medium to large scale manufacturing [17]. A finer grade powder can help to reduce porosity, however, this significantly increases the material feedstock cost and only reduces the scale of porosity rather than remove it. As demonstrated by Azeez et al. [20] for the deposition of Ti-6Al-4V by SLS, a significant improvement in tensile properties was recorded for finer grade feedstock as a consequence of the reduction in porosity preventing dislocation movement and crack initiation.

Several methods are utilised to generate powder feedstocks for AM, the most common include gas atomisation and the plasma rotating electrode process. During the atomisation processes, molten material is fed into an atomisation chamber where high velocity jets are positioned symmetrically around the stream of molten material and used to atomise and solidify the particles. The plasma rotating electrode process is a variation of a plasma atomisation process, whereby a bar of rotating feedstock is fed into the atomisation chamber into the path of co-axial plasma torches and particles are ejected from the spinning molten rod and solidify before hitting the chamber walls. In atomisation processes, powder size can range from 0 – 500 μm and for the plasma rotating electrode process, 0 – 350 μm [22,23]. Dependent on the AM process a different powder size may be required, in the case of SLM 15 – 45 μm is desirable to avoid porosity as previously discussed. Gas atomisation and plasma rotating electrode processes struggle to yield 16% [23] of what is required at this particle size leading to a large volume of ‘low quality’ feedstock. This highlights a further disadvantage of powder-based process in terms of sustainability and economic cost.

2.1.2 Wire Metal Additive Manufacturing

Wire feedstock MAM processes can use either a laser or electric arc energy source to fully melt both the substrate and feedstock. Compared with electron beam and laser powder processes, typically, larger melt pools are generated. WLAM utilises a wire feedstock and laser energy to form fully dense components, where porosity as a consequence of feedstock morphology is prevented [24]. Compared with powder and beam processes, WLAM has been used to deposit at a rate of 48 $\text{g}\cdot\text{min}^{-1}$ [15], which is greater than most powder-based processes. Therefore, it is better suited to creation of small components rather than medium to large scale. The larger melt pools and deposition rate of WLAM leads to a reduction in part fidelity and is more likely to require post-processing as compared to powder deposited equivalent components [14,15]. WLAM has been used to successfully deposit Ti-6Al-4V, for example Dai et al. [25] considered the effects of several laser oscillation paths during deposition to alter the evolution of prior- β grains. Their results demonstrated the successful deposition of Ti-6Al-4V with WLAM, however, no alteration of the prior- β grains was observed. Instead, the development of martensitic α was noted, as a consequence of the high cooling rates associated with utilising laser energy sources.

The most common wire and electric arc MAM process for the deposition of medium to large scale components is WAAM, which finds its origins in arc welding. WAAM can utilise several arc welding energy sources, including metal inert gas (MIG); tungsten inert gas (TIG) and plasma transferred arc (PTA), as well as their variants [14]. In comparison to powder processes or WLAM, WAAM can achieve much higher deposition rates [3]. Whilst material dependent, common deposition rates for WAAM range between 0.75 – 2 kg.hour⁻¹ for titanium alloys [26,27] and 1 – 4 kg.hour⁻¹ for aluminium and steel [14,27]. WAAM deposition is incredibly versatile, being able to produce components from numerous materials including steel [28], aluminium [29], refractory metals such as tungsten and molybdenum [30] and titanium alloys [31]. If a material can be produced in wire form, it is reasonable to suggest that WAAM is capable of its deposition.

Unlike powder processes, porosity as a result of the manufacturing process does not generally occur, unless bad manufacturing controls are employed, for example poor material handling introducing contaminants. Some material exceptions occur, such as the deposition of aluminium alloys, where porosity is particularly challenging due to the contamination from hydrogen which exhibits poor solubility with molten aluminium [32]. Alongside the high deposition rate, the lack of porosity makes WAAM well suited to the creation of medium to large scale structural components. However, because of the high deposition rate, WAAM components are generally referred to as preforms, or near-net shape due to their low resolution [33]. An example of a Boeing 787 structural component deposited with WAAM using titanium alongside the final machined part may be observed in Figure 2-4.



Figure 2-4: Example of Boeing 787 structural component deposited with WAAM using titanium (L) as-deposited (R) post-machining. Reproduced from [13].

In comparison to powder processes, the geometric complexity of the final component cannot be replicated in WAAM. To quantify the low resolution of WAAM deposition, Martina et al. [34] investigated the benefits of PTA deposition of Ti-6Al-4V considering deposition efficiency, i.e. the difference between the effective wall width (usable material) and total wall width deposited. Their results showed a deposition efficiency range from 85 – 98%, dependent on the deposition process parameters, particularly the wire feed speed/travel speed ratio (WFS/TS). A further study by Almeida and Williams [35] supported these results when using a cold metal transfer MIG process, with deposition efficiencies above 80% for varying process parameters and deposition rates in excess of 3 kg.hour⁻¹. It is suggested by Williams et al. [14] that maintaining a medium deposition rate such as 3 kg.hour⁻¹ for steel and 1 kg.hour⁻¹ for titanium and aluminium results in a consistently achievable buy-to-fly (BTF) ratio of 1.5.

In comparison to subtractive manufacturing the WAAM process, in addition to the considerable reduction in the BTF ratio [14], can reduce production time by 40 – 60% and machining time by 15 – 20% [36]. These criteria combined leads to an overwhelming reduction in the cumulative energy demand and associated carbon emission, manufacturing time and total cost. In a cradle-to-gate life cycle assessment conducted by Priarone et al. [37] for the creation of equivalent WAAM titanium, aluminium and steel components compared to subtractive manufacturing, WAAM demonstrated significant reductions in all aforementioned criteria, as may be observed in Figure 2-5.

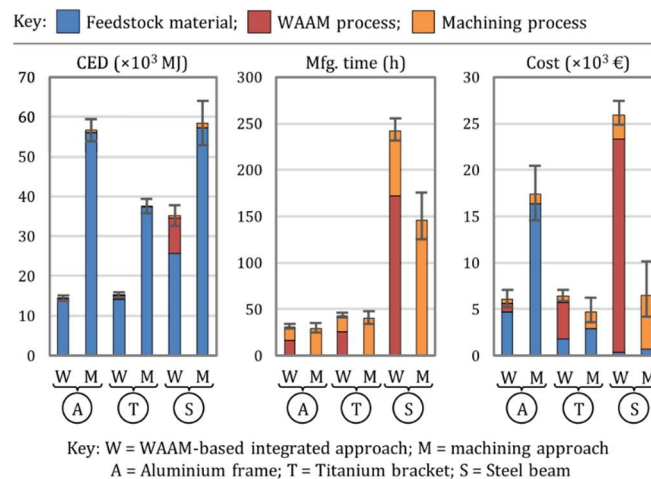


Figure 2-5: Cradle-to-gate life cycle assessment of WAAM versus subtractive manufacturing in terms cumulative energy demand (CED), manufacturing time (Mfg.) and total cost, for equivalent aluminium, titanium and steel components. Reproduced from [37].

2.1.3 Hybrid Additive Manufacturing

It is possible to combine energy sources in what is referred to as hybrid or multi-energy source (MES) systems and is undertaken to combine the advantages of various processes. For example, arc processes deposit at much greater efficiencies and deposition rates than laser processes, however, suffer from poorer geometrical accuracy [2], whereas laser welding processes are able to achieve much more accurate part fidelity [14]. MES systems are capable of combining these distinct advantages to create components at a high deposition rate, with much improved geometrical accuracy [38]. As demonstrated by Chen et al. [39] during the deposition of steel, through the utilisation of a fibre laser coupled to a galvo-scanner and PTA, surface tension was used to spread the deposited material. This MES system allowed the independent control of the energy input and bead geometry, providing configuration of the melt pool geometry for a fixed energy input. The applicability to titanium alloys is yet to be investigated, however, in principle could be applied. In the case of Ti-6Al-4V there may be negative effects on the prior- β grain structure because of the combined total energy negatively affecting the grain size and morphology.

Wang et al. [40] utilised dual stationary lasers to the rear and side of a PTA energy source to elongate the width of the melt pool. As compared to Chen et al. [39], they were unable to dynamically change the width of the melt pool during deposition. However, it is assumed this could be achieved through alteration of the beam diameter ensuring sufficient overlap with the PTA melt pool. They were able to demonstrate the successful MES deposition of Ti-6Al-4V, through the deposition of several small walls of varying thickness. However, they noted a high level of remelting and low process efficiency as a consequence of large quantities of energy focused towards the centre of the melt pool. Despite the lowered individual energy of the heat sources in comparison to a single energy source process, this was likely due to the overlap of the melt pools. Unsurprisingly, their results demonstrated a highly columnar prior- β grain morphology, which is likely attributed to the high heat input.

2.2 Wire + Arc Additive Manufacturing (WAAM)

This research is focused on the use of WAAM, therefore, the fundamentals of the WAAM process are detailed below.

As mentioned in Section 2.1.2, WAAM can employ three welding energy sources, MIG, TIG and PTA [15]. The MIG process utilises the feedstock material as a consumable electrode, to form an electric arc between the wire and substrate. There are four primary metal transfer modes that can be selected: globular; short circuit; spray and pulsed spray, with each displaying distinct characteristics [41]. A modified MIG variant known as cold metal transfer (CMT) was introduced by Fronius International GmbH, lowering the heat input through the retraction of the wire during deposition with a high-speed digital controller to promote droplet transfer. During retraction the current is reduced to near-zero, avoiding spatter and after which the wire is refed and arc reignited [42]. Generally, the benefit of a MIG based process is the capacity to generate high heat inputs to weld thick materials [43], or in the case of additive manufacturing achieve high deposition rates [3]. However, the MIG process is particularly vulnerable to arc wandering, requiring a helical wire to prevent the feedstock sticking and spatter, which leads to inconsistent build geometries, increasing the BTF ratio [44].

The TIG process uses a non-consumable electrode to form an electric arc between the electrode and substrate, in which the wire feedstock material is fed. Either direct current (DC) or alternating current (AC) can be used during the TIG process. AC is generally used for white metals, e.g. aluminium, as the alternating polarity helps to breakdown the oxide formed during deposition [45]. DC can be used as either direct current electrode negative (DCEN) or direct current electrode positive (DCEP) mode. During DCEN mode, the electrode is connected to the negative terminal and in DCEP, the positive terminal. DCEP mode is rarely used, as it can cause the electrode to overheat and burn [46]. The primary advantage of the TIG process is the quality of the weld and precision achievable with high control over the arc when compared to MIG. This makes TIG more suitable for the welding of thinner or additive manufacturing of smaller components, particularly where a lower heat input is required [43]. The trade-off being a lower deposition rate.

PTA is similar in principle to TIG, however, utilises an independent plasma gas that is heated to the point of ionisation, such that it can conduct electrical current. It is then constricted to increase the concentration of ionised particles. The constriction of the arc allows for higher precision and improved arc stability than TIG [47,48]. This increases the process efficiency of the PTA process as compared to the TIG process, making it more suitable to the creation of medium to large scale components [34]. By the design of the enclosed electrode position, the PTA electrode suffers less contamination than TIG, increasing its service life [34]. Figure 2-6 illustrates the design differences between TIG and PTA energy sources (note the effect of arc constriction in the PTA and its effects on arc temperature) [47]. PTA is the additive manufacturing technique of choice for this research project.

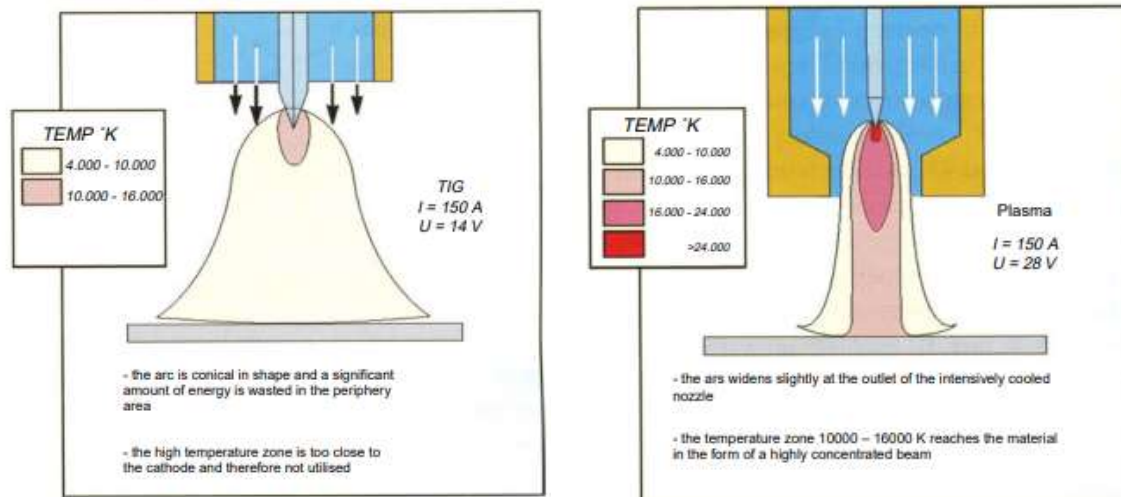


Figure 2-6: Illustration of TIG versus PTA welding arc with respect to arc energy and temperature distribution. Reproduced from [47].

Whilst high deposition rates are beneficial for additive manufacturing, during WAAM large residual stresses congregate as a consequence of the high heat input [49]. Residual stress is induced by the thermal contraction (shrinkage) of the deposited feedstock and substrate material as it cools during solidification [50]. During the inherent thermal cycling of WAAM, residual stresses are alternately accumulated and relaxed during deposition. The distribution of residual stresses is therefore dependent on the process parameters and deposition strategy being implemented [51]. Upon unclamping specimens, it is typical to see a form of distortion, as can be seen in Figure 2-7 during the WAAM deposition of a cruciform structure deposited with Ti-6Al-4V [51].



Figure 2-7: Distortion of Ti-6Al-4V cruciform deposit when unclamped due to residual stress accumulation. Reproduced from [174].

If not addressed, residual stress can lead to cracking during deposition and cooling, particularly where stress concentration factors occur from complex geometrical requirements. Several strategies have been implemented to reduce the amount of residual stress accumulated, as discussed by Mishurova et al. [52], with heat treatments being required for titanium AM deposition. However, Martina et al. [53] demonstrated that residual stress reduction of Ti-6Al-4V could be achieved through interpass rolling, whilst simultaneously refining prior- β grain structure. Additionally, symmetrical building strategies can be implemented to balance residual stress accumulation where the thermal mass is known, as discussed by Williams et al. [14] and Knezovi et al. [54].

Unlike electron beam processes that are deposited within a vacuum chamber, contamination and oxidation must be considered during the WAAM process. Dependent on the reactivity of the deposited material, typically an inert gas such as argon or nitrogen is used for shielding, which has no influence over the deposited material. However, the use of certain shielding gases, such as helium, have been demonstrated to improve the heat extraction and increase cooling rate during the deposition of Ti-6Al-4V [55]. Two forms of shielding exist during additive manufacturing, namely, global shielding and local shielding. Global shielding places the WAAM setup inside an enclosed chamber, which is subsequently purged with the selected shielding gas. This removes the ambient atmosphere, and the oxygen content is monitored within the chamber. Local shielding devices are integrated with the welding torch and generate a local environment of inert atmosphere around the melt pool and surrounding area. They provide positive pressure around the melt pool and recently solidified material to expel ambient air. It has been demonstrated by Ding et al. [56] that laminar flow is essential to prevent mixing with ambient atmosphere which would lead to ineffective protection and oxidation.

2.3 Welding Process Fundamentals

Plasma transferred arc and laser welding have been used during this research project, with the fundamentals of each process characterised in the following sections.

2.3.1 Plasma Transferred Arc

During PTA additive manufacturing an inert gas carrier, typically argon, is fed through an orifice intercepting the tungsten electrode and substrate. It is heated to the point of ionisation by a pilot arc that exists between the tungsten electrode and copper nozzle that surrounds the electrode. As the carrier gas is heated, the random kinetic energy of the molecules exceeds the required ionisation energy, collisions occur between the carrier gas atoms, which strip each other of electrons, forming a neutrally charged mixture of positive and negatively charged ions. This state of matter is referred to as plasma [57]. The plasma gas that now flows out from the copper nozzle orifice, provides a low electrical resistance path between the electrode and substrate, allowing the transfer of the electrical arc [58]. Thus the moniker, plasma transferred arc. The constriction of the plasma leads to a greater arc pressure, temperature and power density as compared to TIG. In addition to the inert plasma gas carrier, PTA torches consist of their own localised shielding gas that flows between the copper nozzle and ceramic nozzle. In practice for additive manufacturing, this does little to prevent oxidation of the melt pool but prevents contamination from floating dust particles at the point of deposition. An illustration of a PTA torch is provided in Figure 2-8.

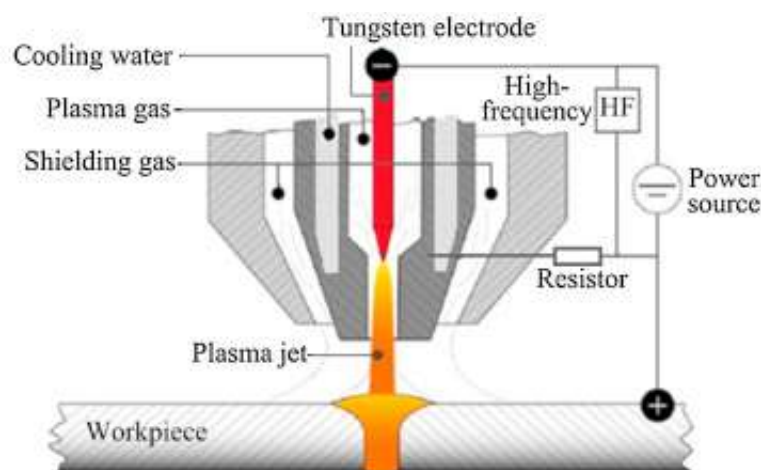


Figure 2-8: Illustration of cross-section of PTA torch. Reproduced from [175].

PTA can be used in two modes of operation, ‘keyhole’ mode or ‘melt-in’ mode, otherwise referred to as ‘conduction’ mode. Keyhole operation is a distinct advantage of the PTA process as compared to other arc welding process. Utilising a high heat input and constriction of the arc, deep penetrative welds can be formed at high travel speeds, as the force of the plasma column displaces molten material [58]. Additionally, for this reason PTA can be used for plasma cutting. Typically, keyhole mode is utilised in square butt welds, where material thickness of 2.4 – 8 mm can be joined with 100% penetration in a single pass [58]. Compared to laser and electron beam welding where keyhole mode can also be achieved, PTA keyhole welding is more tolerant to joint gaps and misalignment [59] as it can generate large melt pool diameters from 0.75 – 3 mm [60]. The stability of the keyhole is primarily dependent on the plasma arc pressure, which determines the heat transfer, and fluid flow within the melt pool [58]. A keyhole may be described as a blind keyhole, where a cavity is formed but has not fully penetrated, an unstable keyhole, where the cavity has fully penetrated but may momentarily close and an open quasi-steady state keyhole, where the keyhole is consistently maintained [58].

More suited to additive manufacturing is the ‘melt-in’ or ‘conduction’ mode which uses lower arc current, plasma gas flow rate and lower electrode setback to de-constrict the arc [58]. This provides a wider melt pool than the keyhole mode and demonstrates similar melt pool characteristics to a TIG melt pool, with the aforementioned benefits of arc stability and electrode protection [34]. During conduction mode the melt pool width is typically wider than the depth of penetration, preventing excessive remelting. The low penetration depth and remelting is a critical factor for applicability to additive manufacturing, making conduction the operating mode of choice. A comparison of the operating modes is presented in Figure 2-9, highlighting the difference in melt pool shape with reference to arc constriction.

As with all energy sources, multiple variants of PTA exist. For example, pulse micro-plasma welding, which utilises arc currents of less than 30 A, has been demonstrated to weld thin film metal sheets of Ti-6Al-4V [61] through the generation of small melt pools. Variable polarity plasma arc welding, otherwise known as AC plasma welding, has been demonstrated to be useful in the deposition of aluminium alloys. The alternating current that is used removes the oxide film that is generated during the electrode positive phase by a process known as cathodic etching [62].

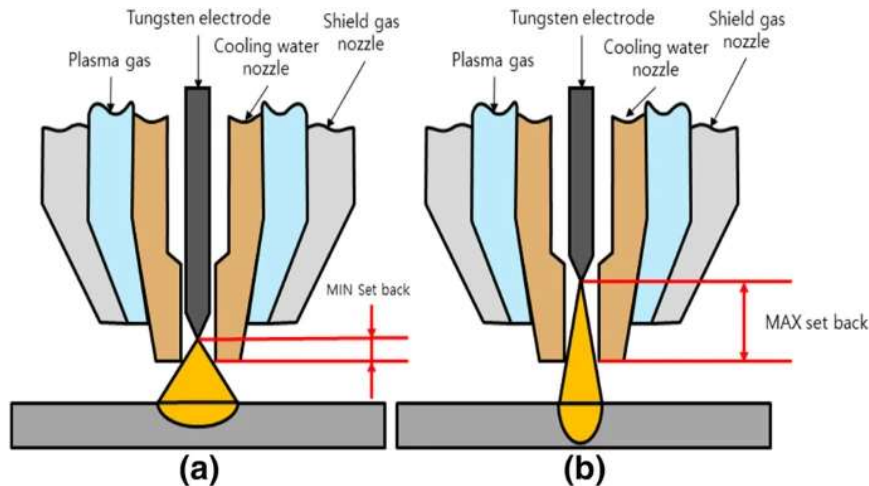


Figure 2-9: (a) Example of conduction mode in PTA (b) Example of keyhole mode in PTA. Note the difference in arc constriction and its effect on penetration depth. Reproduced from [65].

Multiple process parameter considerations are required to be taken into account during WAAM when using PTA. These include:

- Nozzle orifice diameter – The diameter of the orifice of the copper nozzle from which the plasma gas flows directly impacts the constriction of the arc and thus arc pressure. In the Cranfield University WELPC group, an orifice diameter of 3.9 mm has been found to provide minimal defects during WAAM and provide optimum performance [63].
- Tungsten electrode material and size – Tungsten is the primary metal for arc welding electrodes due to its high melting temperature. Electrodes are impregnated with small quantities of alloy elements including thorium, lanthanum and yttrium to provide benefits to arc starting and arc stability. Each type of impregnated tungsten has a maximum permitted current per unit area. It is standard in the WELPC group to use thoriated tungsten, which has a permitted current of 44 A.mm^{-2} [64]. The standard electrode size used at the WELPC is a 4 mm diameter with a 40° electrode tip angle. The tip angle can alter the constriction of the arc, a lower angle gives less constriction, whilst a higher angle provides greater constriction and thus penetration [65].
- Electrode setback – The setback is the distance between the end of the electrode and the nozzle exit. This distance directly impacts the constriction of the arc, a low setback provides less constriction, whilst a high setback, a high constriction. A setback of 2.4 mm is utilised within the WELPC group as standard.

- Composition and flow rate of plasma gas – Typically, pure argon is used as it has a low reactivity with most metals. Mixtures of argon, helium, nitrogen or hydrogen can be used to alter the heat characteristics of the plasma and therefore the melt pool geometry [66]. During the deposition of titanium alloys, it is standard practice at the WELPC to use pure argon, due to its non-reactivity with titanium. Plasma gas flow rate impacts the arc pressure and melt pool shape. As standard a plasma gas flow rate of $0.8 - 1.0 \text{ L.min}^{-1}$ is used within the WELPC.
- Composition and flow rate of shielding gas – The shielding gas used in the PTA torch and through either local or global shielding is important to prevent oxidation and contamination of the melt pool. Typically, a similar gas to the plasma gas is used. In the WELPC, pure argon is used to prevent oxidation of titanium alloys, with $8-10 \text{ L.min}^{-1}$ of torch shielding gas. An oxygen content of $< 4000 \text{ PPM}$ can be used on titanium alloys to prevent detrimental microstructural effects [67], however, an oxygen content $< 1000 \text{ PPM}$ is standard use within the WELPC.
- Contact tip to work piece distance (CTWD) – Due to the constriction of the arc, the arc itself is stiff and this distance is not a sensitive parameter with PTA welding [34]. However, if CTWD is too low, a narrow weld pool and undercut may be observed. If CTWD is too high, the arc penetration and bead geometry may be severely compromised [58]. A CTWD of 8 mm is standard practice within the WELPC.
- Welding current – A variable parameter which controls heat input to the weld. Changes to the heat input alter the bead geometry and microstructure [11,68,69]. Typically, arc currents used during PTA additive manufacturing and welding range from 100 – 300 A, however this is dependent on the material and desired outcome.
- Travel speed – A variable parameter which controls the heat input to the weld. Changes to the heat input alter the bead geometry and microstructure [11,68,69]. During PTA additive manufacturing, the travel speed ranges from $2 - 15 \text{ mm.s}^{-1}$, dependent on the desired heat input, deposition rate or bead geometry.
- Wire feed speed (WFS) – The rate at which material is fed into the PTA during deposition. A variable parameter which is limited by arc energy and travel speed. Process limits exist to ensure bead quality and change in WFS can alter the surface

roughness [34]. Typically, a low WFS provides a better resolution than a fast WFS as it contributes directly to deposition rate [2].

2.3.2 Laser Welding Fundamentals

In comparison to electric arc, laser welding is a relatively new technology. A laser is an incredibly versatile heat source that gives precise control over its energy delivery to the substrate [70]. Unlike arc energy sources, both the energy output and beam size can be manipulated independently, as well as the distribution of the energy within the delivery area [71]. Through the use of optical lenses in the delivery path of the laser, the energy distribution can be manipulated into various profiles, such as top-hat/flat-top, gaussian or doughnut [72]. Other simpler adjustments can be made to alter the energy distribution, for example, through the manipulation of the optical magnification the beam diameter can be altered from microns to millimetres. This level of flexibility allows a wide range of processing conditions to be achieved but, notably, it is the use of a concentrated high energy density that can achieve deep penetration with minimal total heat input, producing comparatively smaller heat affected zones and distortion than arc welding [73].

Laser welding is subject to several common processing challenges including porosity, spatter and setup tolerances. Spatter occurs when droplets of molten material eject from the melt pool, due to emitted metal vapour that causes large acceleration of the melt pool flow. Porosity is more prevalent due to the high cooling rate, low heat input and high depth of penetration, which can cause the entrapment of gases as a consequence of vaporisation. Due to the small beam diameter, it is imperative that the setup of the work piece is highly controlled, fine tolerances mean it is easier to generate defects such as lack of fusion during laser welding as compared to arc welding [73].

Similar to arc welding, during laser welding, two operating modes can be used dependent on the processing parameters, either conduction or keyhole mode [74]. During conduction mode, the melt pool that is generated is shallow and the depth to width ratio is in the order of 1. As energy density increases, it causes vaporisation of the melted material that forms a large depression in the substrate, generating a deep and narrow cavity, this is known as keyhole mode and its depth to width ratio can reach the order of 100 [73]. It has been suggested that a transition mode occurs between conduction and keyhole mode, which can be achieved through the manipulation of the processing parameters, but that it remains

unstable and quickly transitions from one mode to the other [75]. However, this has been disputed and Assuncao et al. [76] demonstrated that no transition mode exists, only a progressive increase in penetration depth and reduction in melt pool width. In the case of additive manufacturing, conduction mode is utilised to prevent excessive remelting and to provide more tolerance to processing defects such as lack of fusion and spatter [77].

In comparison to arc welding, laser welding suffers from a lower energy efficiency due to losses from reflectivity, making the absorptivity a crucial factor [3]. The laser absorptivity will vary dependent on the wavelength of the selected laser; operation mode; surface condition; polarisation and substrate material [78–80]. Several types of lasers exist, including: CO₂; neodymium-ytterbium-aluminium-garnet (Nd:YAG); fibre and diode. The primary factor between the selection of a specific laser is the absorptivity and application [81]. Figure 2-10 presents the laser absorptivity for common metals at various wavelengths. It can be seen that a lower wavelength provides a higher absorptivity than a larger wavelength [82] and therefore requires a lower energy output to generate an equivalent power density. The greater absorptivity of fibre lasers, which have wavelength of 1.07 μm , make them more versatile than CO₂ lasers, which have a wavelength of 10.7 μm . Fibre lasers are more attractive for additive manufacturing, particularly in the case of highly reflective materials such as copper [82]. Additionally, the low wavelength of fibre lasers mean they do not interact with silica glass, enabling them to be delivered through optical fibres, making their setup versatile [82]. For these reasons fibre lasers are commonly used in the WELPC as they are well suited to additive manufacturing process requirements.

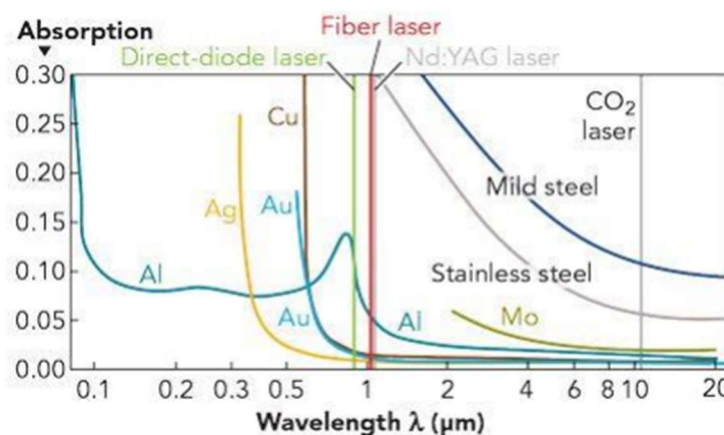


Figure 2-10: Absorptivity in metals as a function of laser wavelength. Reproduced from [176].

The surface condition of the substrate material must also be taken into account, as this can affect the absorptivity. The absorptivity of the material can be altered by the level of oxidation present on the substrate as demonstrated by Kwon et al. [83]. Their study identified a temperature dependent absorptance during fibre and CO₂ laser deposition when considering titanium and steel alloys as compared to aluminium. When using the fibre laser, in the case of titanium and steel, above 700°C, they identified an increase in absorptivity, as a result of oxidation [84]. This highlights the importance of maintaining an oxygen free environment during the additive manufacturing process to ensure process stability. In the case of aluminium, no oxidation was observed and thus the absorptance did not vary with temperature. Their results may be observed in Figure 2-11.

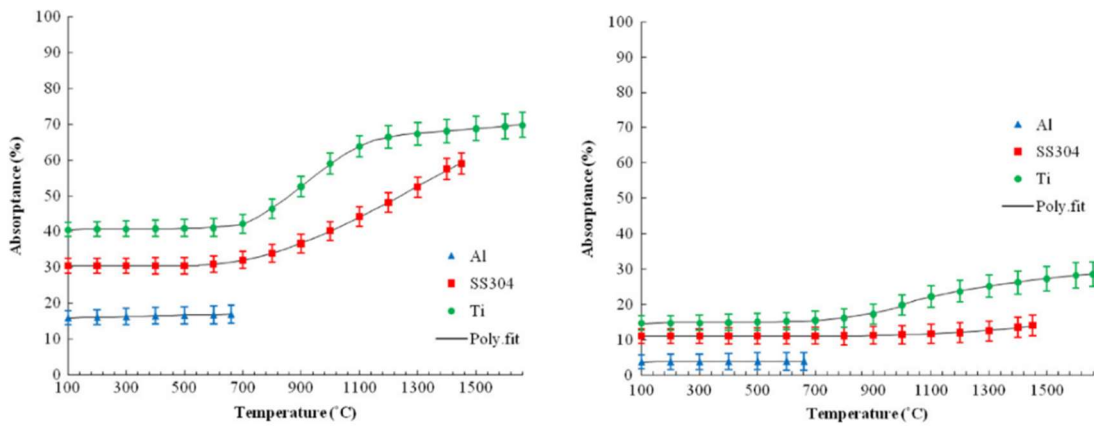


Figure 2-11: Laser absorptivity for aluminium, stainless steel and titanium as a function of temperature for (L) fibre laser with wavelength 1.07 μm (R) CO₂ laser with 10.7 μm wavelength. Reproduced from [83].

Absorptivity is also affected by the operating mode i.e. conduction or keyhole. When a laser is operated in conduction, the absorptivity is lower than if operated in keyhole mode. As the penetration of melt pool becomes deep, the absorptivity increases significantly, as a consequence of internal reflections within the melt pool, as the laser cannot escape. As demonstrated by Katayama et al. [85] in Figure 2-12, as power density was increased and the operating mode transitioned from conduction to keyhole, an increase in the absorptivity from $\sim 30 - 90\%$ was observed. The effect of laser polarisation becomes more prevalent in keyhole welding mode as it dictates the reflectivity of the incident radiation. Dependent on the angle of incidence and polarisation state of the laser beam, more or less energy can be absorbed, changing the penetration depth of the keyhole [82] as demonstrated in Figure 2-13.

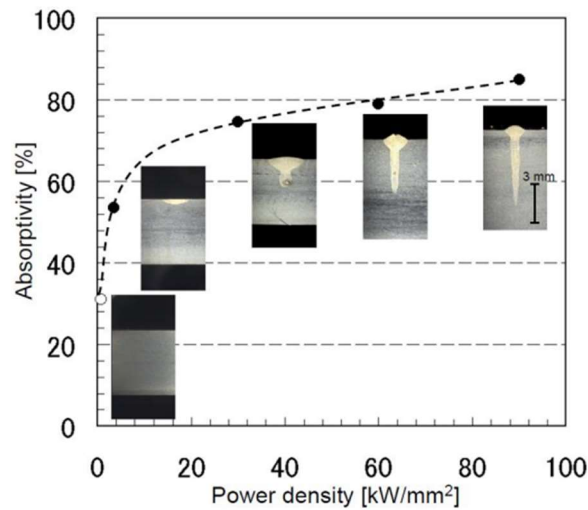


Figure 2-12: Laser absorptivity as a function of power density. Note the significant increase in absorptivity as operating mode transitions from conduction to keyhole. Reproduced from [85].

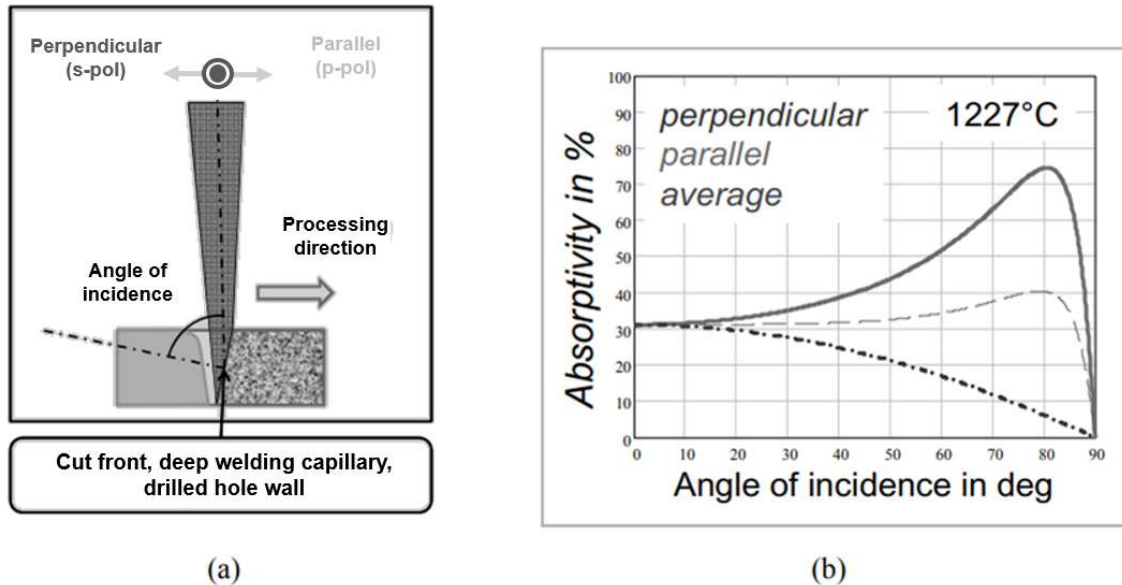


Figure 2-13: (a) Sketch of typical laser-material interaction and melt pool geometry during keyhole mode (b) Absorption coefficient in Fe for p- and s-polarisation state. Reproduced from [177].

In the case of additive manufacturing of Ti-6Al-4V using fibre lasers and wavelength of $1.07 \mu\text{m}$, numerous absorptivity coefficients have been identified. For example, Cook and Ritchie [86] reported an absorption coefficient as low as 27% during a Ti-6Al-4V powder fusion process. The result is surprising given the propensity for powders to internally reflect the laser between particles improving absorptivity. Keller et al. [87] in contrast, reported an absorptivity of 40 – 55%, taking into account variable radiation losses for a Ti-6Al-4V powder fusion process and, seemingly in agreement, Kaplan [88] reported an average absorption coefficient for titanium at $1.07 \mu\text{m}$ of 44%. In this research a

absorption coefficient of 45% was used to calculate the delivered laser energy based upon this existing literature.

In comparison to arc welding processes, once a laser and absorptivity are identified, the process parameter selection for laser additive manufacturing considers less variables. The primary considerations to be made during laser AM include laser power; travel speed of deposition; beam diameter and energy distribution profile. The energy profile can be manipulated by optics which alter the distribution of the energy within the beam diameter, giving much more precise control than arc welding [3]. Typically, gaussian profiles are utilised, however, top-hat/flat-top and doughnut can be used in specific applications, these profiles may be observed in Figure 2-14. During this research a gaussian beam profiled was utilised.

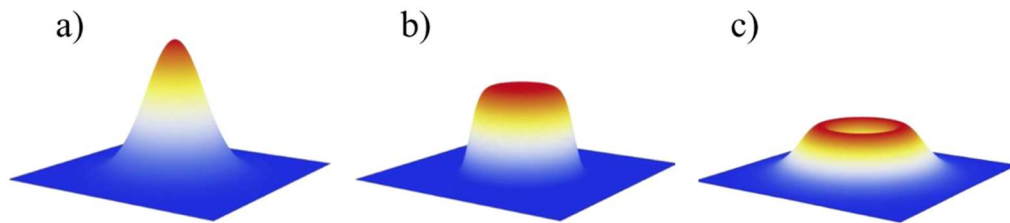


Figure 2-14: Examples of various energy profile distributions delivered by laser through manipulation of internal optics (a) gaussian profile (b) top-hat/flat-top (c) doughnut. Adapted from [72].

2.3.3 Thermal Efficiencies

When considering the efficiency of an additive manufacturing process, either arc or laser based, the energy transfer and melting efficiencies are taken into account [82]. For an additive manufacturing process to be considered efficient, a large proportion of the energy output should be used to generate the melt pool, rather than transferred to the heat affected zone (HAZ) or environmental losses. In the case of additive manufacturing, an increase in the deposition rate for an equivalent energy output, the better the process efficiency [3]. There are several efficiencies to consider during additive manufacturing.

The energy transfer efficiency or coupling efficiency, considers the distribution between the total applied power (P_a) and the power transferred to the workpiece (P_t). The difference between them occurs due to environmental power losses. In laser-based processes this is primarily related to reflected energy and in arc-based processes occurs due to radiative and convection energy loss from the arc to the surrounding area. In the case of PTA processes a proportion of energy is also dissipated through the copper nozzle and electrode [3]. This relationship is illustrated in Figure 2-15.

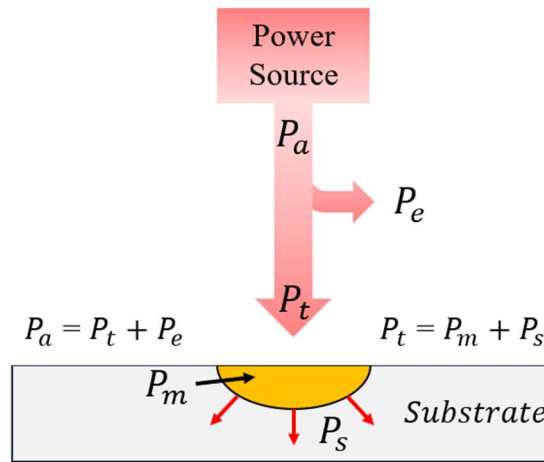


Figure 2-15: Illustration of applied power (P_a), power transferred to workpiece (P_t), power used to generate a melt pool (P_m) and power losses through environment and substrate (P_e and P_s). Adapted from [3].

The energy transfer efficiency is calculated through Equation 2-1 [89]. In arc welding processes it is referred to as the arc efficiency, and laser processes, the absorptivity or coupling coefficient. The energy transfer efficiencies are generally measured using calorimetric methods and are well known, particularly in arc-based processes [90–92]. It has been identified for arc processes that the arc efficiency can vary dependent of the type of power source used. MIG welding exhibits an arc efficiency as high as 0.84, followed by TIG processes between 0.67 – 0.8 and PTA between 0.47 – 0.75 [90–93]. In this research, an arc efficiency of 0.6 was used on the recommendation of The Welding Institute and previously described literature for PTA welding. Generally, reflectivity is less of an issue for arc welding processes compared to laser and therefore exhibits higher energy transfer efficiency.

$$\eta_{ET} = \frac{P_t}{P_a} \dots \dots (2-1)$$

As depicted in Figure 2-15, the power transferred to the substrate can be further separated into the power used to generate the melt pool (P_m), and the power conducted through the substrate (P_s) in the form of heat loss by conduction. The ratio between the power used to generate the melt pool and the power transferred to the substrate is referred to as the melting efficiency and is calculated via Equation 2-2 [3].

$$\eta_{ME} = \frac{P_m}{P_t} \dots \dots (2-2)$$

During additive manufacturing, to ensure process efficiency and reduction in the required energy output, a high melting efficiency is desired. Additionally, this reduces the potential for unwanted defects such as a large HAZ, residual stress and distortion [91]. The process parameters used can alter the melting efficiency, for example an increase in welding speed increases the melting efficiency whilst an increase in arc current decreases melting efficiency [94]. Additionally, the shape of the tungsten electrode has previously been identified to alter the arc constriction [65] and plasma gas composition [55], which in turn can alter melting efficiency [94].

Ultimately, the process efficiency can be expressed as the ratio between the energy required to generate the melt pool and the total applied power, which can be calculated by Equation 2-3 [3]. It may be observed this is a combination of the energy transfer efficiency and melting efficiency. To ensure high quality additively manufactured deposits in Ti-6Al-4V, the process parameters selected must ensure the melting efficiency, thus, process efficiency is high. This ensures that the grain structure is not significantly altered in previously deposited layers through conduction losses and excessive remelting, as the energy transfer efficiency is ultimately fixed through consistent deposition conditions and energy sources.

$$\eta_{PE} = \eta_{ME} \cdot \eta_{ET} = \frac{P_m}{P_a} \dots \dots (2-3)$$

2.4 Solidification Theory

During MAM the solidification conditions that exist differ across processes and ultimately dictate the final microstructure and thus mechanical properties. In the case of WAAM and the deposition of Ti-6Al-4V, the solidification behaviour is responsible for the morphology of the α and prior- β grain structures which may be observed through

microscopy. In the case of Ti-6Al-4V, there is a solid-state phase transformation from $\beta \rightarrow \alpha$ phase at $\sim 980^\circ\text{C}$ when cooling. The solidification conditions of interest in this research are during the solidification of the β phase, which will be discussed in the following section.

In order for a material to solidify from a liquid to solid phase there must be a reduction in Gibbs free energy, i.e. a driving force towards solidification [95,96]. When a material begins to cool from a liquid state, there is not an instantaneous change of state. There must be nucleation of solid particles within the melt pool. Nucleation can occur in two forms, homogenous nucleation or heterogeneous nucleation. Homogenous nucleation occurs when a nucleus forms spontaneously and at random within the bulk molten material. Heterogeneous nucleation occurs from an existing boundary, for example foreign particles, impurities or substrate wall. Heterogeneous nucleation dominates in WAAM of Ti-6Al-4V as it requires significantly less free energy and undercooling as compared to homogenous nucleation [97].

During the growth of a nucleus within the melt pool, two competing energies exist, the volume free energy of the solid and liquid, G_s and G_L respectively [98,99,104]. For solidification to occur, the volume free energy change in Equation 2-4 of the molten material must be negative, which means when the melt pool temperature drops below the equilibrium melting temperature, there is a driving force towards solidification [98,104].

$$G_s - G_L = \Delta G_V \dots \dots (2-4)$$

Considering homogenous nucleation, when a nucleus forms there is an additional energy related to the solid-liquid interface. This acts as a barrier to nucleation as energy is required to maintain this interface [95]. As the surface area of the nucleus increases, the energy required to maintain this interface also increases. If the nucleus is assumed spherical, the total energy of the system can be expressed in Equation 2-5, where $\Delta G_{n(HOM)}$ represents the total free energy (during homogenous nucleation) and γ as the surface energy at the solid-liquid interface [98,99]. This is expressed graphically in Figure 2-16.

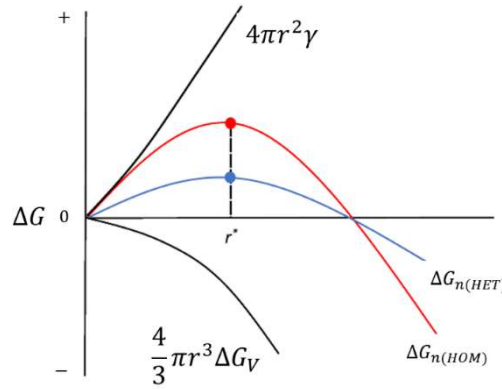


Figure 2-16: Total free energy change during solidification of a nucleus for both homogeneous and heterogenous nucleation. Note that as a nucleus's radius increases, the volume free energy decreases and surface free energy increases. Adapted from [178].

$$\Delta G_{n(HOM)} = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma \dots \dots (2-5)$$

As a nucleus grows, the volume free energy decreases and the surface energy between the solid-liquid interface increases, acting as a barrier to nucleation. As nucleation occurs, the total free energy increases, however, there comes a critical point where the total free energy decreases and the nucleus becomes stable. The size of the nucleus at this point is known as the critical radius, this is the required radius required for a nucleus to survive and grow, below this radius and the nucleus will dissolve back into the melt pool [98,104].

Considering heterogenous nucleation, a nucleus is no longer spherical within the melt pool, instead the nucleus forms at an existing boundary, which alters the surface free energy. The surface free energy term must now consider several interactions between the solid-liquid interface (σ_{SL}), boundary-solid interface (σ_{BS}) and boundary-liquid interface (σ_{BL}), represented by Young's equation [100] in Equation 2-6. Where θ represents the wetting angle between the boundary and solid-liquid interface, as illustrated in Figure 2-17.

$$\sigma_{BL} = \sigma_{BS} + \sigma_{SL} \cos(\theta) \dots \dots (2-6)$$

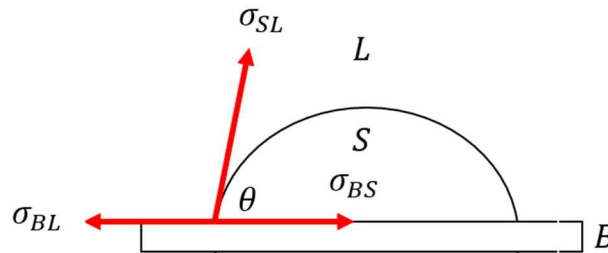


Figure 2-17: Illustration of heterogenous nucleus forming at an existing boundary and respective solid-liquid interactions. Adapted from [178].

The change in surface energy alters the total free energy of this system as can be expressed in Equation 2-7 [98], where $\Delta G_{n(HET)}$ represents the total free energy during heterogenous nucleation and $S(\theta)$ is the shape factor in relation to the wetting angle. The shape factor is always less than 1, meaning the effective energy barrier to nucleation is lower during heterogenous nucleation than in homogenous nucleation [96], as observed in Figure 2-16. Therefore, homogenous nucleation is a rarely observed and heterogeneous nucleation dominates, particularly in WAAM, where there are foreign particles and the substrate to nucleate from.

$$\Delta G_{n(HET)} = \left(\frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \sigma_{SL} \right) S(\theta) \dots \dots (2-7)$$

A further important factor that can alter the total free energy is the amount of supercooling, particularly constitutional supercooling. The lower the temperature of the molten material compared to the melting temperature, the greater the driving force for nucleation as the energy barrier is lowered [98].

Constitutional supercooling refers to the difference in temperature between the molten material and liquidus temperature of an alloy [95], and the temperature gradient within the liquid [101]. Unlike pure metals which have a single freezing point, alloys begin to solidify at the liquidus temperature (T_L) and fully solidify by the solidus temperature, this creates a freezing range. As an alloy solidifies it expels solute into the liquid melt as a consequence of solute partitioning, assuming minimal diffusion and mixing within the liquid phase as a consequence of fast cooling rates, the local composition (C_L) and thus liquidus temperature at the solidification front are deviating from the bulk [102]. The ratio between the solidus composition and liquidus composition is represented by the partition coefficient (k) [103]. Dependent on the actual temperature gradient (T_G) of the melt pool, the area created by the difference in the liquidus temperature and thermal gradient is referred to as the constitutionally supercooled zone [104], as is illustrated by Figure 2-18. The larger the area of constitutional supercooling, the lower the energy barrier to nucleation [95,96]. However, whilst this makes the potential for homogenous nucleation more likely to occur, so too does it lower the energy barrier for heterogenous nucleation.

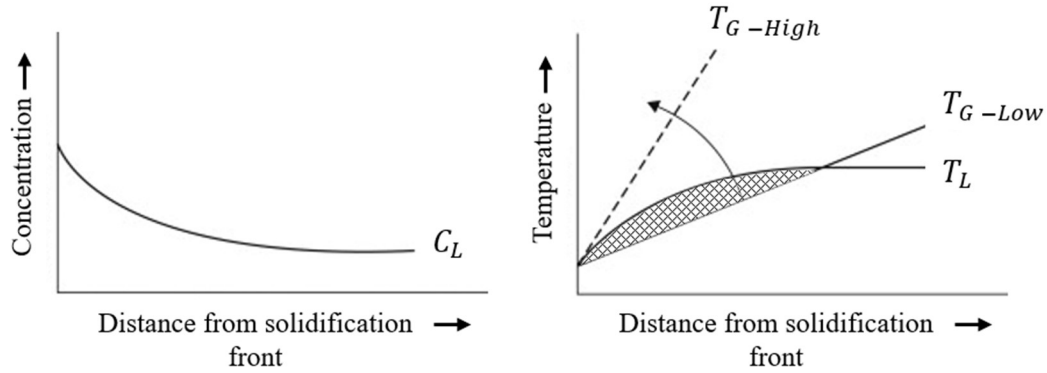


Figure 2-18: Illustration of the variation in (L) melt pool composition at the solidification front (R) liquidus temperature and thermal gradient with respect to distance from the solidification front. Note the hatched area of constitutional supercooling. Adapted from [102].

Generating constitutional supercooling in Ti-6Al-4V during MAM is difficult, with both a high thermal gradient and lack of solute partitioning [105,106]. Solute partition coefficients of aluminium and vanadium in titanium are close to unity, meaning they do not expel solute during solidification. With coefficients of 1.01 – 1.13 and 0.89 – 0.96 for aluminium and vanadium respectively [107,108], little constitutional supercooling can exist [106] making prior- β grain refinement challenging.

Following the nucleation process is growth, whether from a homogeneous or heterogeneous nucleus. Growth occurs from the relative solidification front and extends into the melt pool. The combination of the thermal gradient and growth rate determines whether a nucleus grows from a planar solidification front or whether it grows as a protrusion into the liquid as either a cellular or dendritic structure [102,109,110]. The growth rate can be defined as the rate at which the solidification front moves into the melt pool and is also relative to the shape of the melt pool [111,112]. In the case of additive manufacturing and the advancement of a moving melt pool, the solidification rate can be equated to the travel speed during deposition [113] and the melt pool curvature, perpendicular to the solidification relative to the direction of deposition [114]. The thermal gradient is constituted by the temperature variation between two points within the melt pool, which ultimately relies upon the deposition material of choice, its thermophysical properties and the process parameters utilised. The effect of the thermal gradient and growth rate on growth morphologies is illustrated in Figure 2-19. Kobryn and Semiatin [115] demonstrated it was possible to move around this solidification map for Ti-6Al-4V and deposit equiaxed dendritic grain structures in Ti-6Al-4V during metal-mold casting and directional solidified castings. However, they were not as successful

during powder and laser additive manufacturing. Whereas others such as Bermingham et al. [113] have garnered more success in WAAM through manipulation of the growth rate. Prior- β grain refinement techniques will be discussed later.

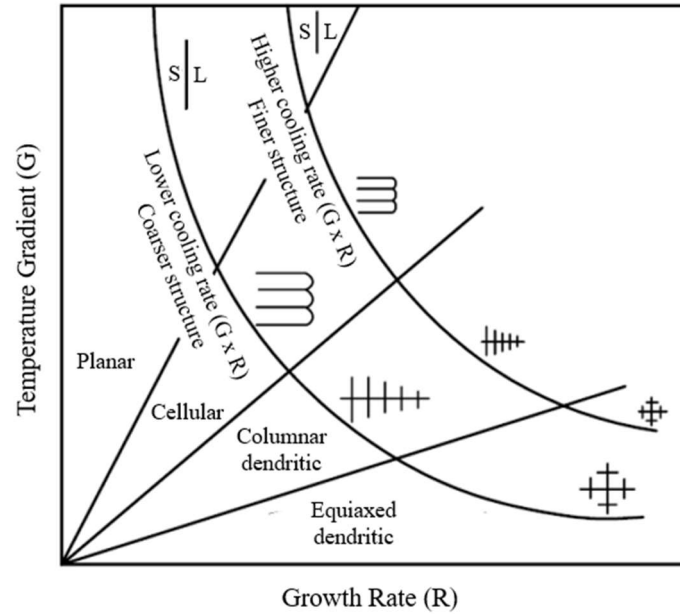


Figure 2-19: Effect of temperature gradient (G) and growth rate (R) on the size and morphology of growth during solidification. Adapted from [179].

In the case of Ti-6Al-4V deposited using WAAM, it is not possible to determine the growth morphology of Ti-6Al-4V directly, due to the $\beta \rightarrow \alpha$ phase transformation which eradicates evidence of cellular or dendritic growth [116], other than it being columnar as evidenced by the lack of competitive growth and columnar prior- β grains that are typical of WAAM [106,113,117,118]. However, Bermingham et al. [116], was able to confirm that dendritic rather than cellular growth took place during WAAM of Ti-6Al-4V through the addition of trace amounts of boron, which was rejected at the dendrite tips during solidification, highlighting the dendritic prior- β grain structure under room temperature conditions when analysed by electron microscopy.

Due to the lack of constitutional supercooling generated during the WAAM deposition of Ti-6Al-4V, as a consequence of its composition and high thermal gradients, a columnar dendritic structure dominates, leading to the development of columnar prior- β grains observed [106,113,118–120]. Growth occurs via a heterogenous and epitaxial growth mechanism, whereby atoms readily attach themselves to the partially melted pre-existing lattice of the previously deposited layer [111]. It is prominent in WAAM for Ti-6Al-4V prior- β grains to orientate themselves around the $\langle 100 \rangle_{\beta}$ orientation, leading to highly

textured deposits in line with the build direction [113,118,121–123]. This is due to the dendrites gaining a growth advantage when following the maximum thermal gradient perpendicular to the solidification front, suppressing less competitive dendrites [124]. In the case of WAAM, the maximum thermal gradient is almost vertical from the bottom of the melt pool to the torch, due to the relatively shallow melt pool depths. Additionally, the preferred growth orientation of BCC metals grows most favourably along the $\langle 100 \rangle$ direction [124]. Combining these factors provides the columnar prior- β grain structure and $\langle 100 \rangle_\beta$ texture an overwhelming growth advantage.

2.5 Titanium Alloys

The discovery of titanium can be traced back to 1791, when British Mineralogist, William Gregor discovered iron-titanium oxide (FeTiO_3), coined ‘ilmenite’. Several years later, German chemist Martin Heinrich Klaproth, was able to isolate titanium oxide (TiO_2) [125]. However, it would not be until 1932 when Justin Kroll developed a method to commercially extract titanium (with a process still in operational use today), through the reduction of TiCl_4 with magnesium [126]. A significant volume of research has been conducted to explore alternative processing techniques for titanium, to reduce the processing costs, however this has shown low throughput and unacceptable oxygen contamination in comparison to the Kroll’s process [127,128].

The primary consumer of titanium is the aerospace industry, with an increasing concern to reduce weight. Reduction in weight leads to a reduction in fuel load, reducing carbon emissions and running costs [125]. Titanium competes directly against aluminium, with both being considered light metals. Titanium has a density of 4.51 g.cm^{-3} , twice that of aluminium, however, benefits from several distinct attributes: a high specific strength (including at high temperature); corrosion resistance and galvanic compatibility with composites [125,126]. Conversely, in comparison to aluminium, titanium and its alloys suffer from expensive extraction and processing costs as discussed and is therefore manufactured in a batch rather than continuous process like other structural metals [126].

Research into titanium alloying has led to the development of three titanium classes: α , $\alpha + \beta$ and metastable β , which refer to the atomic structure of the alloy at room temperature. The most widely applied titanium alloy is the $\alpha + \beta$ Ti-6Al-4V, which accounts for the largest proportion of the titanium market [125,126]. Titanium alloy applications include

biomedical, as a consequence of their low chemical reactivity and high strength-to-weight ratio [129], structural components such as landing gear support structures; fuselage and wing rings [130] and gas turbine engines, occupying approximately 1/3 of structural weight [126]. The latter enabled by the development of α alloys, allowing increased operating temperatures before degradation due to oxidation and high temperature creep [126].

2.5.1 Classification of Titanium Alloys

The first titanium alloys were introduced in the 1940's, including the major Ti-6Al-4V, that accounts for the largest percentage of titanium alloy applications today [2,125,126,130]. Titanium alloys are categorised as α , $\alpha+\beta$ or β , dependent on the crystallographic structure at room temperature [125,131] and contain different alloying elements to influence the final crystallographic structure, dependent on the desired microstructural and mechanical response. The alloying elements used are therefore classified as either α , β or neutral stabilisers. To understand the effect of an alloying element, first consider pure, un-alloyed, titanium. It exists as an allotropic element, exhibiting β phase above $\sim 882^\circ\text{C}$, before undertaking a solid-state phase transformation to α phase below this temperature, known as the β transus [125,131]. α stabilisers increase the β transus temperature, hence stabilising the α phase, whereas β stabilisers decreases the β transus temperature, hence β stabilisers.

Primary α phase stabilising elements include aluminium; oxygen; nitrogen and carbon. β stabilising elements can be separated into two distinct groups, isomorphous and eutectoid. Isomorphous β stabilisers include molybdenum and vanadium, which have total solubility with titanium, whereas eutectoid β stabilisers include copper, nickel and iron elements which have the potential to form intermetallic compounds with titanium [125,126,131]. Neutral elements have no effect on the β transus temperature and include alloying elements such as: zirconium and tin. Their purpose is to alter mechanical properties through mechanisms such as solid solution strengthening [125]. The effect of the different stabilisers is illustrated in Figure 2-20.

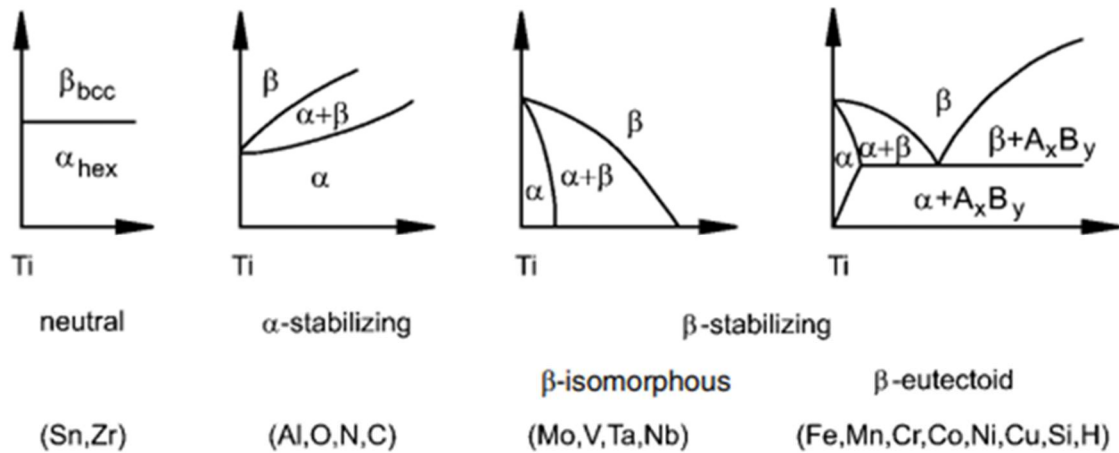


Figure 2-20: Effect of α , β or neutral stabilising elements on the β transus temperature and phases present.
Reproduced from [141].

The α and β phase refer to the crystallographic structure. α phase exists as a hexagonal close packed (HCP) structure and β phase exists as a body centred cubic (BCC) structure. The difference in these structures and their total volume fraction, contributes to the difference in mechanical properties of titanium alloys [125,126,131]. The crystal structure of the HCP and BCC unit cells are illustrated in Figure 2-21.

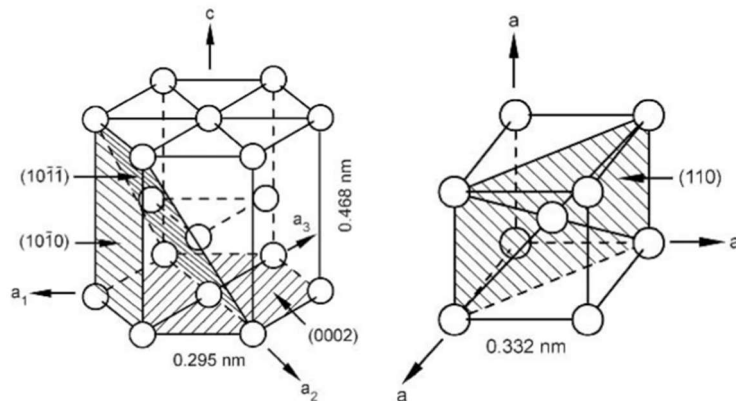


Figure 2-21: (L) HCP unit cell of α phase (R) BCC unit cell of β phase.
Reproduced from [125].

A major difference between the HCP and BCC phases is the ease of plastic deformation. This comes as a consequence of the number of available slip systems most favourable towards plastic deformation. The number of available slip planes in HCP equates to 3, as compared to 12 for the BCC unit cell. These slip systems relate to the densely packed planes which allow dislocations to move more easily. The HCP unit cell has a packing density of 74% and BCC 68%, therefore HCP is expected to deform more easily, as dislocations can more freely move. However, the energy required for plastic deformation is also related to the minimum slip length. In the HCP unit cell this is equal to 1, whilst

for BCC this equates to 0.87, therefore, plastic deformation is more favoured in the BCC unit cell [126].

The α phase HCP unit cell is intrinsically anisotropic due to a lack of symmetry and is demonstrated by the Young's modulus of an α phase titanium single crystal, with a variation between 100 GPa and 145 GPa when loaded parallel or vertical to the basal plane $\{0001\}_\alpha$ respectively [126]. Additionally, the lattice parameters of the titanium HCP structure are $a = 0.295$ nm and $c = 0.468$ nm, which gives a c/a ratio of 1.587 compared to the ideal HCP ratio of 1.633. This ratio can be increased through the inclusion of interstitial elements and substitutional elements with smaller atomic radii than titanium atoms [126]. The reduced c/a ratio leads to slip being favoured on the prism planes as a consequence of the increased packing density of the prism planes relative to the basal planes.

As titanium cools from the β to the α phase, a solid-state phase transformation occurs under a fixed relationship known as Burger's orientation relationship (BOR) [132]. BOR is characterised by the following crystallographic relationships: $\{0001\}_\alpha // \{110\}_\beta$ and $\langle 1120 \rangle_\alpha // \langle 111 \rangle_\beta$, observed schematically in Figure 2-22.

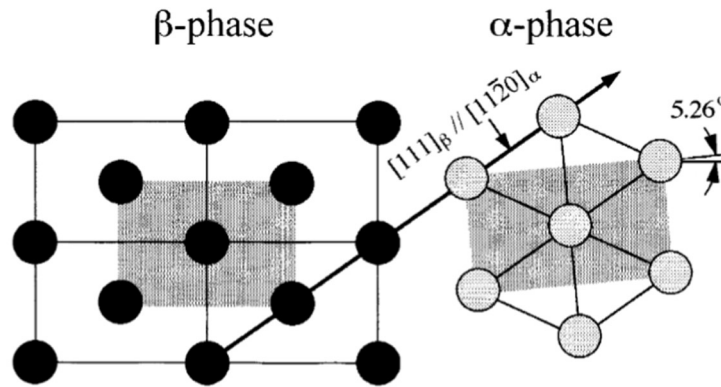


Figure 2-22: Illustration of Burger's orientation relationship in relation to the $\{110\}_\beta$ and $\{0001\}_\alpha$ planes. Reproduced from [180].

A total of 6 slip planes and 2 slip directions in the BCC β phase means there is a maximum of 12 variants available when transforming to HCP α [125,132]. This relationship is extremely useful when conducting prior- β grain structure analysis of titanium alloys with electron backscatter diffraction analysis (EBSD). EBSD is a direct crystal orientation measurement technique that utilises secondary electron microscopy (SEM). First introduced in 1987, it has now become the standard representation technique for

crystallographic analysis and grain structure analysis [133], which is used to classify titanium alloy microstructures.

In order to conduct EBSD of a titanium specimen, it is first placed inside of an SEM and inclined at angle $\sim 70^\circ$ relative to the electron beam and detector, with a phosphor screen (which converts scattered electrons to light) placed horizontally several millimetres from the sample surface. As electrons are fired towards the surface of a sample, dependent on the local crystallographic orientation of sample being analysed, the electrons are diffracted in a cone towards the phosphor screen and interact to generate diffraction patterns. These diffraction patterns can be resolved by Kikuchi bands, in the regions of high electron intensity to resolve the crystallographic orientation and phase of the sample at a localised position [133,134]. An example of the diffraction patterns associated with various cubic orientations may be observed in Figure 2-23.

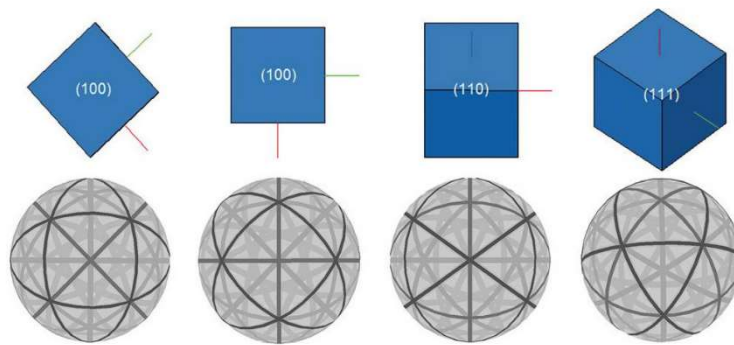


Figure 2-23: Diffraction patterns generated by various crystallographic orientations of a cubic structure captured during EBSD analysis. Reproduced from [181].

EBSD does have limitations as the quality of diffraction pattern acquisition is highly dependent on the surface quality of the specimen being analysed [134]. Additionally, to achieve a high-quality capture, despite automated imaging which speeds up the technique, the interaction volume is of a relatively small size, meaning there is an intensive resource requirement to map large surfaces. In the case of Ti-6Al-4V, the allotropic nature of the alloy means that at room temperature, where EBSD is conducted, the material exhibits an α phase morphology. In order to characterise the prior- β grain structure, it is possible to convert the α phase data captured during EBSD into reconstructed β phase data due to BOR. With respect to BOR, 12 possible α variants may exist during the $\beta \rightarrow \alpha$ transformation [135,136]. The prior- β grain orientation can be determined from the most likely parent orientation for each α variant in turn [137] based upon the analysis of

misorientations between adjacent points either side of an α variant boundary of which a limited number of α/α misorientations exist when inherited from the same prior- β grain [138,139]. This method is automated and for this research project was conducted via a MATLAB script provided by the Henry Royce Institute at the University of Manchester (as a partner of the project) based upon the methods described by Davies [138] and Davies et al. [137].

2.5.2 Properties of Titanium Alloys

The effect of alloying elements on titanium alloys and their implication on α , β or $\alpha+\beta$ classification, has a profound impact on the mechanical properties. This is primarily determined by the phase volume fraction and microstructure. α alloys contain less than 5% β , $\alpha+\beta$ alloys contain 10 – 20% β and β alloys contain more than 20% β [140]. The general primary characteristics and examples of different titanium alloys are discussed below.

Commercially pure titanium (CPTi) is an α alloy that is primarily used inside harsh, corrosive environments due to its high levels of corrosion resistance. This makes it attractive to the biomedical and chemical industry [129]. Despite being referred to as ‘pure’, CPTi does contain low levels of some alloying elements and is therefore categorised by grade. Strength is not the primary concern for CPTi alloys, however, it can be improved through the increase in oxygen content to provide interstitial hardening [125]. The tensile strength of α alloys ranges from 240 MPa – 740 MPa [126].

Near- α alloys are used in high operating temperature environments of 500°C - 550°C. These alloys combine the high strength properties of $\alpha + \beta$ alloys with superior creep resistance [125]. Near- α alloys limit the maximum aluminium content to 6%, to prevent stress corrosion. The most widely used near- α alloy is Ti-6Al-2Sn-4Zr-2Mo, which can be further alloyed with small quantities of silicon, which precipitates at high temperature, pinning dislocations in place and improving strength. Generally, all near- α alloys contain small traces of silicon [126]. As near- α alloys typically operate in high temperature conditions, it can be challenging to prevent oxidation and α -case hardening leading to embrittlement as oxygen is absorbed [67].

The most commonly used titanium alloy is the $\alpha + \beta$ Ti-6Al-4V, accounting for more than 50% of titanium alloy usage globally [125,126,131,141]. $\alpha + \beta$ alloys are the most

versatile titanium alloy, offering a balance of strength, ductility and fracture toughness. This has made Ti-6Al-4V one of the most developed titanium alloys to date. Unlike α or near- α alloys, $\alpha + \beta$ alloys are susceptible to creep and embrittlement at elevated temperatures, making their use somewhat limited in applications such as aeroengines [125]. Similar to near- α alloys, further alloying additions can be made such as the introduction of silicon to impede dislocation movement.

β alloys are generally characterised by high tensile strength greater than 1400 MPa due to large quantities of solid solution strength hardening alloying elements. This leads to a specific strength comparable with high strength steels and aluminium alloys. For example, during the development of the Boeing 777, 17-4PH high strength stainless steel castings were replaced in favour of Ti-15V-3Cr-3Al-3Sn despite its lower strength due to the considerable weight savings of $\sim 35\%$ [130]. Due to their complex microstructures, metallurgists have freedom to optimise metastable β alloy mechanical performance [126]. However, the use of β alloys, such as Ti-5Al-5Mo-5V-3Cr, may be limited due to their high specific weight, poor weldability and poor oxidation behaviour [126]. Additionally, the complex thermal histories during WAAM can lead to undesirable α phase precipitation [142].

2.5.3 Ti-6Al-4V

Ti-6Al-4V is the primary alloy investigated in this research and as such, further consideration of its properties and microstructure is presented.

Ti-6Al-4V has a melting point of 1670°C and β -transus temperature of $\sim 980^\circ\text{C}$ [125], varying slightly dependent on the actual alloy constitution. The cooling rate from the $\beta \rightarrow \alpha$ phase plays a significant role in determining the final α microstructure achieved at room temperature. Four types of microstructures can be achieved: equiaxed; lamellar; bi-modal and martensitic [143] with each having distinct properties. Lamellar structures have been demonstrated to provide better fatigue characteristics, impeding crack propagation through increased crack path tortuosity [144]. Equiaxed microstructures provide improved resistance to crack initiation, but poorer crack propagation characteristics as compared to lamellar structure [145]. Bi-modal α microstructures combine crack initiation and propagation resistance to provide all round improvement to fatigue characteristics [143]. Finally, martensitic α , increases the tensile strength and

hardness, whilst simultaneously reducing plasticity [146]. The thickness of α laths, otherwise known as the inter-lamellar spacing (ILS) is proportional to the effective slip length and has been demonstrated to play an important role on the mechanical properties of Ti-6Al-4V [125].

Upon cooling through the $\beta \rightarrow \alpha$ phase transformation, slow cooling rates lead to nucleation and growth via a diffusion-controlled process, whereas high cooling rates lead to martensitic α through a diffusionless transformation. In the case of WAAM deposition of Ti-6Al-4V, a complex thermal history exists as a consequence of the consistent reheating of previous layers during deposition. This leads to complex and inconsistent α morphologies throughout a single build and variation in ILS [140].

Considering the phase diagram for Ti-6Al-4V in Figure 2-24, after complete solidification and above the β -transus temperature of $\sim 918^\circ\text{C}$ only the BCC β phase is present. As the material is slowly cooled α begins to transform (following BOR) initially at the β grain boundaries, which act as nucleation sites. The α phase continues to grow into the prior fully β grains forming colony α whereby the α lamellar form a parallel relationship and small amounts of β phase are retained [147]. As the cooling rate increases, the size of the α colonies is reduced and the thickness of the α lamellar is reduced. In order to minimise elastic strain within the grain interior as cooling rate increases, new α lamellar nucleate on the long face of existing α and grow perpendicularly to form the characteristic ‘basketweave’ microstructure seen in WAAM and known as Widmanstätten α [125,148]. Dependent on the alloying content the amount of α and β phase will vary. In the case of Ti-6Al-4V as the material continues to cool, β will continue to transform to α following BOR until room temperature, where only a small quantity of $< 5\%$ is retained.

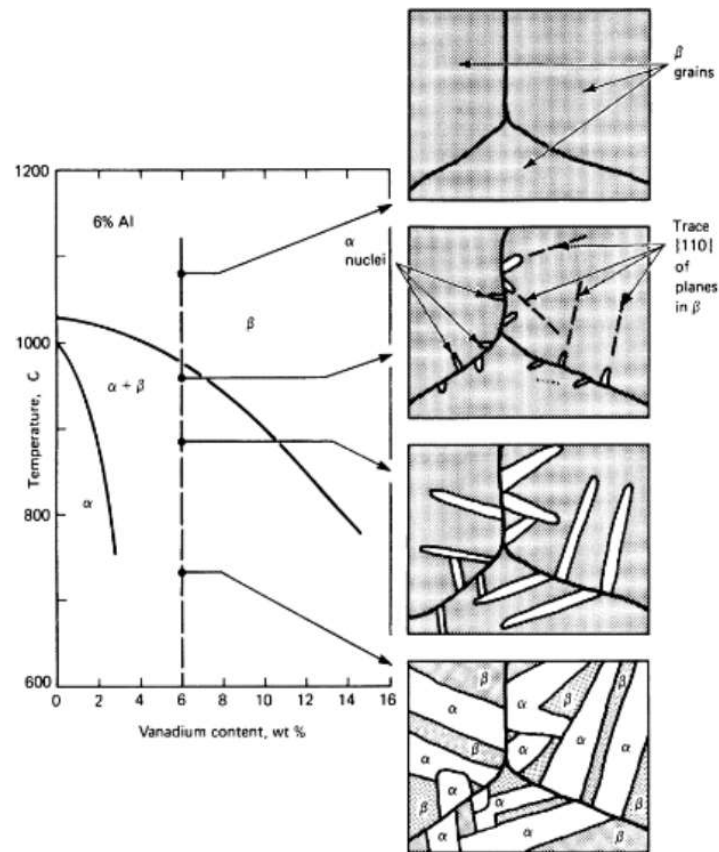


Figure 2-24: Diagrammatical representation of a microstructure evolution of Ti-6Al-4V with respect to temperature. Reproduced from [147].

Lamellar microstructures are observed as platelets that grow from prior- β grain boundaries into the grain perpendicularly. Typically, this structure is referred to as Widmanstätten or basketweave, which occurs when growing platelets collide and new α laths nucleate. The new laths begin to grow almost perpendicular to the original lath. This is self-regulating and occurs to minimise elastic strain [125]. Dependent on the cooling rate, the thickness of the α laths can be altered. A slower cooling rate leads to thicker laths, whilst a higher cooling rate leads to finer laths [149]. This is the most common form of microstructure seen in WAAM for Ti-6Al-4V [140].

A bi-modal microstructure consists of an α and β matrix, which contains a mixture of primary α grains and areas of transformed β containing secondary α lamellae. The size of each constituent can be manipulated by specific heat treatments [150]. Fully equiaxed microstructures contain predominantly primary α grains with no areas of secondary α lamellae and retained β phase at grain boundary triple points [151]. Finally, martensitic α microstructures are observed as fine, needle like lamellar. To achieve the bi-modal or equiaxed structures in additively manufactured Ti-6Al-4V, deformation and heat treatment are required [140], unlike lamellar or martensitic structures. Martensitic microstructures are more prominent in laser additive manufacturing than WAAM, which exhibit faster cooling rates [152], which predominantly exhibits lamellar microstructures [118,153]. Examples of each microstructure morphology may be observed in Figure 2-25.

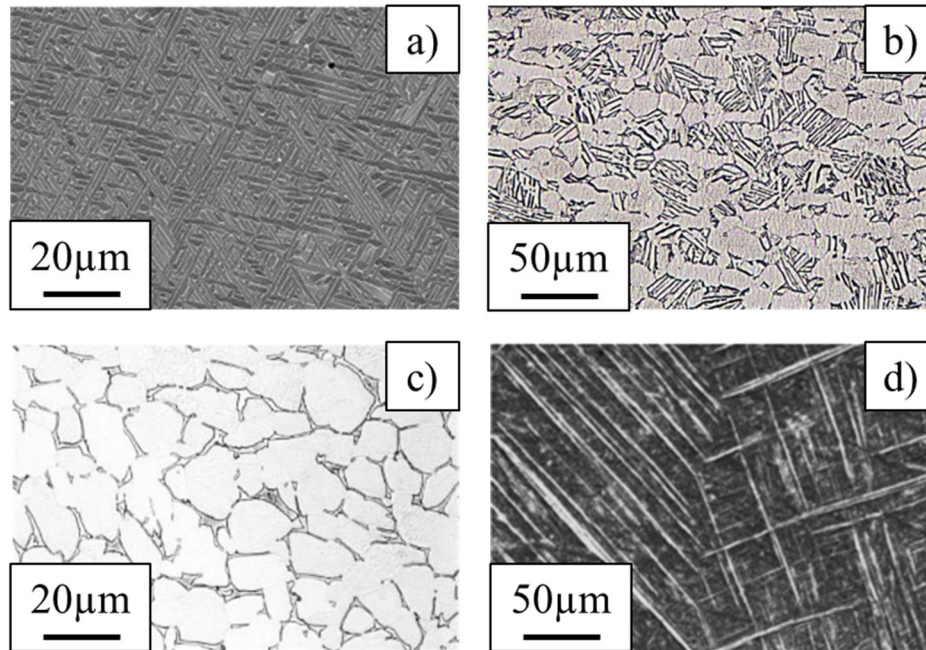


Figure 2-25: Examples of microstructures observed in Ti-6Al-4V a) Lamellar (Widmanstätten) [153] b) Bi-modal [182] c) Equiaxed [125] d) Martensitic [152].

As previously mentioned, the mechanical properties and the microstructure directly correlate with one another. In the case of the lamellar microstructures of $\alpha + \beta$ Ti-6Al-4V deposited with WAAM, this is related to the size of ILS and width of α colonies (where α lamellae stack neatly against one another in the same direction), but also the size and morphology of prior- β grain boundaries [125]. The prior- β grain boundaries play an important role within WAAM of Ti-6Al-4V, which transforms into continuous grain boundary α (α_{GB}) and acts as the nucleation site for the initial solid-state transformation,

which first occurs as α colonies before Widmanstätten α [154]. The dimensions of colony width and ILS determine the effective slip length, which alters the movement of dislocations and therefore the mechanical response as may be observed in Figure 2-26.

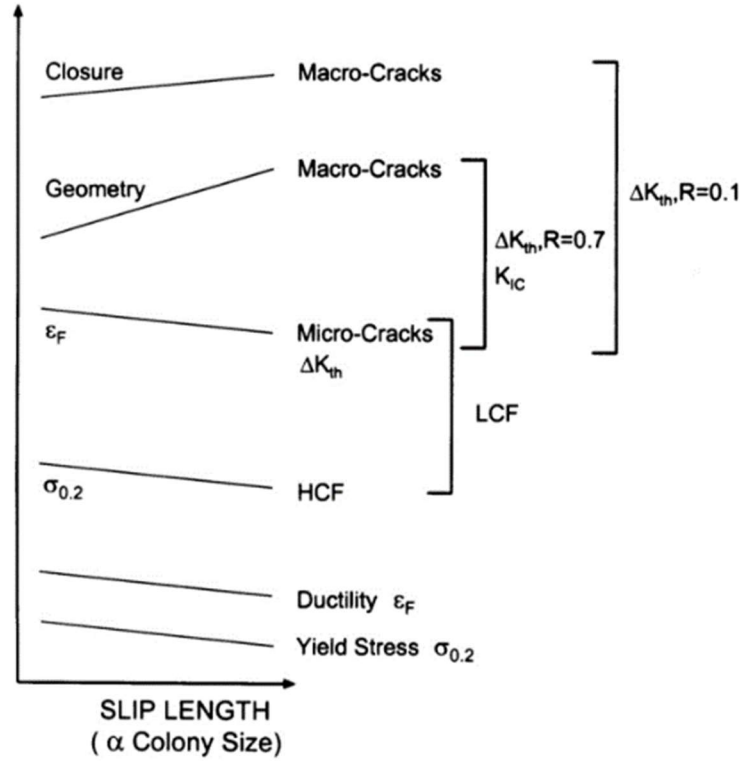


Figure 2-26: Effect of effective slip length on the mechanical properties of Ti-6Al-4V. Reproduced from [125].

During the phase transformation from $\beta \rightarrow \alpha$ during cooling, α_{GB} is the first to transform along the β/β grain boundaries maintaining BOR [155], colony α nucleates from the α_{GB} , before the formation of the α Widmanstätten morphology [154]. This means that the prior- β grain structure plays an important role in the overall mechanical response in addition to the α microstructure obtained. For Ti-6Al-4V manufactured with WAAM, there is the propensity for the creation of large columnar prior- β grains [14,106,118]. These grains extend from the bottom to the top of WAAM deposits and are highly textured $\langle 100 \rangle_\beta$ in relation to the build direction [34,115,118,156]. The proportion of the α_{GB} ; colony α and Widmanstätten α therefore differs in the horizontal and vertical directions.

During WAAM Ti-6Al-4V deposition there is a low level of constitutional supercooling which exists due to a low level of solute partitioning from the aluminium and vanadium alloying elements [157]. When combined with the high thermal gradients associated with the WAAM process this leads to an epitaxial growth mechanism, whereby, atoms attach themselves to the pre-existing partially melted lattice of the grain below [117], as this requires substantially lower free energy as compared to homogenous nucleation ahead of the solidification front [158]. In relation to the α microstructure that nucleates from the prior- β grain boundaries, it can be determined why prior- β grain refinement is required to prevent plastic heterogeneity in the loading directions [4]. This is a consequence of the inequitable distribution of grain boundary α and colony α in various loading conditions [159]. An example of the unfavourable columnar prior- β grain morphology and texture may be observed in Figure 2-27.

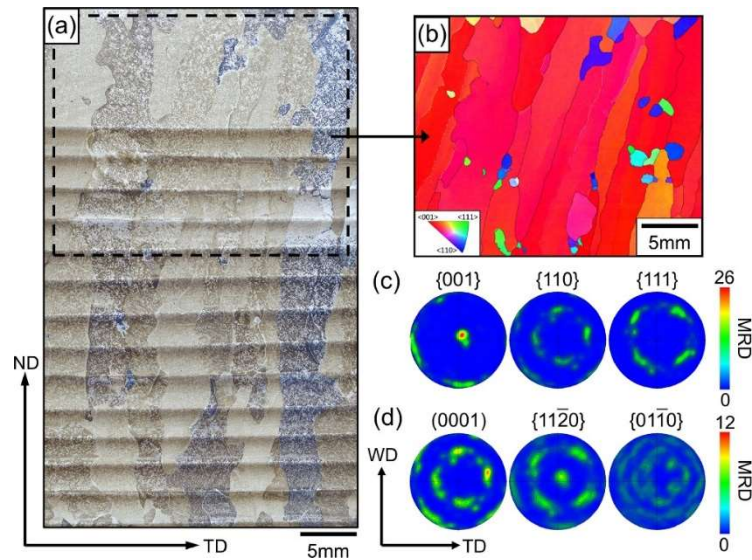


Figure 2-27: Example of columnar prior- β grain structure obtained during WAAM deposition of Ti-6Al-4V with highly textured $\langle 100 \rangle_{\beta}$ preferentially orientated grains. a) Optical macrograph b) reconstructed prior- β with inverse pole figure colouring with respect to the build direction c) prior- β cubic pole figures d) α HCP pole figures. Reproduced from [183].

The effect of the columnar orientated prior- β grains may be observed primarily in the horizontal and vertical loading directions when subject to tensile testing. Wang et al. [118] demonstrated that the average yield strength and ultimate tensile strength (UTS) across 18 specimens, varied from ~ 800 MPa and ~ 925 MPa respectively in the vertical direction to ~ 875 MPa and 975 MPa in the horizontal direction. Greater divergence was seen in the ductility of the specimen varying from $\sim 14\%$ in the vertical direction to $\sim 9\%$ in the horizontal direction, a direct consequence of crossing varying proportions of prior- β grain boundaries. This shows agreement with other studies such as Neto et al. [160], who would

later go on to pursue machine hammer peening as a mode of prior- β grain refinement due to the columnar prior- β grains. However, in comparison to Wang et al. [118], Neto et al. [160] exhibited a yield strength and UTS of ~ 800 MPa to 900 MPa respectively in the vertical direction as opposed to ~ 850 MPa to ~ 925 MPa in the horizontal direction, whilst ductility ranged from $\sim 20\%$ in the vertical to 12% in the horizontal. The difference in the tensile strength and ductility between the two studies is a consequence of acute compositional and microstructural differences in the walls deposited. As discussed, in $\alpha + \beta$ the tensile strength is controlled by solid solution strengthening, interstitial solute level, ILS spacing and colony α volume fraction [125], all of which differ between the studies. Regardless, as expected a consistent difference in the horizontal and vertical loading directions is observed, that requires correction during WAAM of Ti-6Al-4V.

2.5.4 Prior- β Grain Refinement of Ti-6Al-4V during WAAM

Given the plastic heterogeneity observed in WAAM Ti-6Al-4V deposits, the refinement of prior- β grains has been a priority for the deposition of Ti-6Al-4V. Multiple methods have been investigated to achieve this, including cold-working [123,161]; alloy modification [119]; inoculation [4] and melt pool agitation [162,163]. All of which have the goal to refine the prior- β grain morphology and crystallographic texture to ensure an isotropic mechanical response. An overview of these methods is discussed in the following section.

The most common cold-working methods include rolling [161] and peening [123]. The principle behind these methods is to induce a plastic strain into the material. During the subsequent reheating of successively deposited layers, this provides a driving force for potential recrystallisation of the β grains during solidification. This method has shown substantial success in the refinement of prior- β grains and texture. Both Donoghue et al. [161] and Martina et al. [122] have been able to demonstrate the effect of rolling on the prior- β grain structure, which shows a complete breakdown in the $\langle 100 \rangle_\beta$ preferred growth orientation and columnar morphology. The size of grains can be directly correlated to the applied load and profile of the rolling tool either flat or profiled. Martina et al. [122] reported prior- β grain sizes of 125 μm and 139 μm for a profiled and flat roller respectively for a 50 kN applied force and 89 μm and 56 μm for a 75 kN applied force. The drawback of the rolling method is the strain becomes localised in the centre of the

deposit, therefore, an outer skin of non-refined prior- β grains is obtained as recrystallisation occurs at the centre [122,161]. This may be observed in Figure 2-28.

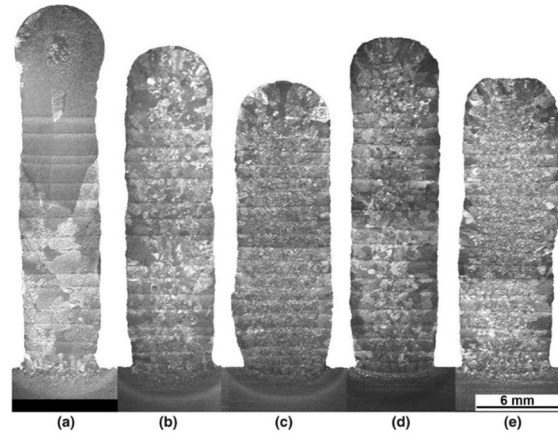


Figure 2-28: Optical macrographs reproduced from Martina et al.[122], considering the effects of rolling on WAAM Ti-6Al-4V a) as-deposited b) 50 kN profiled roller c) 75 kN profiled roller d) 50 kN flat roller e) 75 kN flat roller. Note the skin of unrefined prior- β grains.

Nonetheless, the recrystallisation and refinement of the prior- β grains in the centre leads to the removal of the texture in WAAM Ti-6Al-4V manufactured components. As discussed by Addison et al. [26] who considered interpass rolling to refine prior- β grain structure, the tensile results now show greater homogeneity with a reported yield strength of 1020 MPa and 995 MPa in the horizontal and vertical directions respectively, and 1075 MPa and 1075 MPa UTS and 13% and 13% elongation. The peening mechanism is equivalent to that of the rolling mechanism, however, instead of a large rolling rig being required, the surface of the substrate is struck with an indentation tool at high frequency. The setup of the peening tool gives much more freedom than rolling, as it can be attached to a robotic manipulator and peening can be conducted at higher travel speeds upwards of 18 mm/s [160]. Unlike the large applied forces of rolling, which induce an additional decrease in the size of α lamellae as well as prior- β grain size, no such effects are reported in peening, a likely consequence of the smaller applied force [160].

Alloy modification and inoculation involves the addition of further alloying elements to Ti-6Al-4V to increase the level of solute partitioning, to promote constitutional supercooling and nucleation ahead of the solidification front [117], or to provide grain growth restriction and particles which act directly as nucleation sites to encourage competitive dendritic growth [4,164]. Boron has been used by several researchers [119,165,166] to provide prior- β grain refinement in this manner. Bermingham et al. [119]

demonstrated that some refinement can be achieved in relation to the prior- β grains, however, they still remained predominantly columnar. The addition of the boron as a prior- β grain growth restrictor was successfully demonstrated, with noticeably finer columnar prior- β grains present. The addition of the boron was found to be more successful in reducing the volume of colony α being replaced with TiB intermetallic regions. Other researchers such as Kennedy et al. [167] studied the use of titanium nitride (TiN) and yttrium (Y) particles to encourage grain refinement. Similar to Bermingham et al. [119], the addition of Y led to a reduction in grain width rather than inducing a columnar to equiaxed transition. However, the addition of the TiN particles led to a substantial prior- β grain refinement leading to an equiaxed morphology of 300 μm size grains. The challenge of this method of refinement is two-fold, the experimental setup to ensure the entrapment of the particles in the melt is inherently unstable, with powder being blown away by arc pressure and the formation of intermetallic compounds which may result in detrimental mechanical properties relative to the application.

Agitation of the melt pool to refine the prior- β grains has demonstrated efficacy in powder processes [163], whereby acoustic cavitation is generated within the molten material and triggers nucleation ahead of the solidification front to block epitaxial growth. Whilst this method does not prevent the underlying epitaxial growth, it encourages homogenous nucleation ahead of the solidification front where none existed prior. This mode of refinement has recently been applied to laser + wire additive manufacturing process by Yuan et al. [162] and has showed promising results in the final deposited layers. It is reliant on a mechanism similar to Todaro et al. [163], through inducing cavitation to promote nucleation ahead of the solidification front in the melt pool and dendrite fragmentation, however, instead of an ultrasonic manipulator, steel tooling is used not dissimilar to a peening tool [160] to cause vibration. Whether this method is applicable to WAAM is yet to be seen, however, in principal it shows promise, but further considerations are required, such as the difference in melt pool flow dynamics etc. Additionally, melt pool agitation for prior- β grain refinement has focussed on powder processes where components are small, whether this can be applied to components 10's of kilograms larger deposited with WAAM remains to be seen.

In the as-deposited condition little success has been demonstrated in the refinement of prior- β grains. Only when process limits have been pushed to extremes has some level of

refinement been achieved. Wang et al. [168] stumbled across prior- β grain refinement through the increased deposition rate for a fixed arc energy during deposition of Ti-6Al-4V. However, it was reliant on an unstable deposition condition [169], whereby the feedstock maintained continuous penetration of the melt pool surface. This led to heterogenous nucleation at the surface of the un-melted wire before breaking away into the melt pool and blocking epitaxial growth. This was later confirmed by Wang et al. [170] whom deliberately penetrated the melt pool with the feedstock wire to induce refinement. However as discussed by Rios et al. [169] this form of wire transfer should be avoided on the basis of being inherently unstable, with the potential to form lack of fusion defects, skittering along the bottom of the melt pool and damage to equipment. Fundamentally, the mechanism of refinement cannot be identified, the prior- β refinement achieved is likely a combination of dendrite fragmentation, heterogeneous nucleation and agitation of the melt pool to activate nucleation ahead of the solidification front [162].

Others such as Zhang et al. [171] and Bermingham et al. [113] have attempted to alter the deposition strategy or processing parameters to induce prior- β refinement and demonstrated limited success. Zhang et al. [171] alternated the deposition speed and arc energy independently across alternating layers, utilising epitaxial growth of refined grains solidified at the top of the melt pool to grow from the bottom of the subsequent layer. This prevented the $\langle 100 \rangle_\beta$ preferentially orientated grains. However, this is not without limitation. A continual change in ILS, whilst not reported, would likely be observed as a consequence of the fluctuation in cooling rate as a consequence of changing heat input [11]. Additionally, variations in bead geometry would make deposition of large scale components and complex features difficult. Meanwhile, Bermingham et al. [113] attempted to manipulate the solidification velocity through increasing the travel speed of deposition. However, they were unsuccessful in achieving refinement due to a negative impact on the thermal gradient as bead geometry was altered as the WFS/TS ratio was changed [34].

Recently, researchers have attempted to incur prior- β grain refinement through recrystallisation above the β transus temperature via heat treatment. However, to enable this there must be stored plastic energy within the material to provide the potential for recrystallisation during the heat treatment. Wang et al. [172], attempted prior- β grain refinement through the alteration of deposition strategy through reduction of the

interlayer dwell time. Whilst, demonstrating limited success, some prior- β grain refinement occurred from recrystallisation of the prior- β grains. This was a consequence of stored energy within α martensite that was generated due to the increased cooling rate as interlayer dwell time was reduced. However, martensitic structures are largely avoided during WAAM of Ti-6Al-4V [173] due to their brittle mechanical properties and additional challenges when achieving the required large cooling rates in the as-deposited condition such as residual stress. Additionally, the practicalities of maintaining the pre-deposition temperatures required to influence the cooling rate to such an extent on larger WAAM builds has yet to be demonstrated. Therefore, it is not typical to see prior- β grain refinement during a heat treatment process of an as-deposited Ti-6Al-4V built component with WAAM as little plastic stored energy exists. Instead cold-working is used to induce the plastic strains necessary which recrystallises during what is essentially a heat treatment in the successively deposited layer [122,161].

2.6 Research Gap

The refinement methods described in Section 2.5.4 represent the common methods required to achieve the refinement of prior- β grains in the as deposited condition. Each process provides clues as to the requirements of being able to achieve prior- β grain refinement in the as-deposited condition. For example, the requirement for constitutional supercooling, or lack thereof highly restricts the potential for prior- β grain refinement. The need for stored plastic energy to drive potential recrystallisation. The promotion of nucleation ahead of the solidification front through induced cavitation. Or in the as-deposited condition when the melt pool is agitated to provide nucleation ahead of the solidification front through dendrite fragmentation or heterogenous nucleation from the penetrating feedstock to block epitaxial growth.

For the refinement of prior- β grains in the as-deposited condition, translation into direct process control based upon a stable processing condition does not yet appear to have been achieved. When refinement is achieved, the mechanism responsible is not clearly distinguishable. It could be nucleation ahead of the solidification front to block epitaxial and textured growth due to a reduction of thermal gradient, through melt pool agitation as a consequence of the feed stock penetrating the melt pool surface, the introduction of

heterogenous nucleation along the penetrated feedstock or dendrite fragmentation at various points in the melt pool as a consequence of the two aforementioned mechanisms.

Additionally, the current refinement techniques add further constraints to design freedom and incur an increased capital cost and lead time to the WAAM process. Therefore, this highlights a suitable gap in the existing literature, to achieve prior- β grain refinement in the as-deposited condition whilst utilising a stable processing condition i.e. not reliant on inherently unstable melt pool penetration [169] and identification of the refinement mechanism, which currently cannot be explicitly identified in the studies where prior- β grain refinement in the as-deposited condition has been achieved.

2.7 References

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3. Refinement of Ti-6Al-4V Prior- β Grain Structure in the As-deposited Condition via Process Control during Wire-Direct Energy Deposition.

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Abstract

This study demonstrates that refinement of the prior- β grains generated during the wire-direct energy deposition of Ti-6Al-4V was achievable whilst maintaining a stable processing condition in the as-deposited condition, not reliant on penetration of the feedstock to the melt pool. Previous studies on prior- β grain refinement of Ti-6Al-4V have been reliant on either post-processing, alloy modification or agitation of the melt pool to achieve refinement. Through process control alone, it was identified that an increase in the deposition rate for a fixed energy input led to a reduction in the specific energy density of deposited material. Utilising pyrometry, it was determined that the reduction in the specific energy density led to a decrease in the thermal gradient, measured using a linear thermal gradient approximation, encouraging apparent homogenous nucleation within the melt pool. Whilst maintaining a stable ‘droplet’ transfer mode, the gradual reduction in specific energy density transformed the grain structure from the typical columnar morphology through a mixed morphology to an equiaxed grain morphology; confirmed via prior- β grain reconstructions and inverse pole figure analysis made possible by electron back scattered diffraction microscopy of the deposited samples. Microhardness measurements demonstrated larger variations in the refined prior- β grain specimens as compared to the columnar as a result of more complex α morphologies generated.

3.1 Introduction

Additive manufacturing (AM) is a technique used to create near-net shape components through the successive layer-by-layer deposition of a feedstock material. Typically, such near-net shape components require little or no post-processing [1]. Several distinct AM processes exist, each having unique benefits and drawbacks. They are characterised by feedstock and energy source, therefore labelled a wire or powder-based process using an arc, laser or electron beam heat source, or, some combination to form a hybrid process. One such process is Wire + Arc Additive Manufacturing (WAAM), which has the potential to rival conventional forgings [1,2]. WAAM is a direct energy deposition (DED) process where a wire feedstock is fed directly into an electric arc heat source attached either to a computer numerical control (CNC) gantry or robotic manipulator in overlapping weld deposits to form a single homogenous component. This process produces significantly reduced material wastage when compared to the traditional subtractive manufacturing of a billet, whilst providing comparable mechanical properties [2–5]. However, the deposition is best described as a preform which typically requires some element of machining before service [6].

WAAM flourishes in the manufacturing of medium to large scale components, benefiting from a low capital investment requirement and readily available welding wire feedstock [2,7,8]. It is possible to deposit most types of material, from common metallics such as steel and aluminium to refractory metals such as tungsten and molybdenum [2,9]. WAAM is applicable to the deposition of titanium alloy preforms, particularly Ti-6Al-4V, a common material in the aerospace industry within airframe and aeroengine applications due to its high specific strength, corrosion resistance and electromechanical compatibility with composites. WAAM is ideally suited for the creation of titanium components, due to the cost of extraction, processing and machineability of titanium [10] by reducing the typical buy-to-fly ratio of 10 – 20 to < 1.5, and reducing manufacturing lead times from months to mere hours [2]. However, limitations do exist. WAAM processes suffer from high heat accumulation leading to complex thermal histories and residual stresses that effect grain structure and mechanical properties [11,12]. Additionally, titanium has high chemical affinity with oxygen, requiring the use of local or global shielding devices to

avoid embrittlement known as α -case hardening that impacts ductility and crack initiation properties, particularly at the outer surface [13,14].

A major limitation of Ti-6Al-4V WAAM components is the epitaxially developed prior- β grain structure in the as-deposited condition, in which a coarse textured columnar grain structure is present, typically extending from the bottom to the top of the deposit [15], resulting in significant mechanical anisotropy and fatigue behaviour [16–21]. To refine this unavoidable columnar grain structure of Ti-6Al-4V requires the promotion of nucleation ahead of the solidification front, i.e. homogenous nucleation, which for Ti-6Al-4V process control is typically avoided due to the innate lack of favourable solidification conditions. Instead, investigators have typically focused on external forms of manipulation including alloy modification, melt pool agitation and mechanical processing.

Alloy modification can be used to alter the chemical composition of the deposit to refine grains in several ways. Nucleation ahead of the solidification front can be promoted through the introduction of elements that provide greater solute partitioning, thus constitutional supercooling. The alteration of the feedstock material to include such elements to alter the liquidus temperature, increases the size of the ‘mushy’ zone, encouraging competitive randomly orientated dendritic growth in the segregated compositionally rich solute. The introduction of growth restricting elements such as boron [22] prevents already nucleated grains from growing further, limiting their size and encouraging random competitive dendritic growth. The inoculation of the melt pool by introducing foreign particles or elements [20], which in addition to increasing the size of the ‘mushy’ zone, act as nucleation sites for competitive growth. Whilst alloy modification has been successful in refinement of grains, highlighting the importance of increasing the constitutional supercooling, it can lead to the deposition of ‘dirty’ alloys, where these trace elements have a high probability to form detrimental secondary phases, limiting application [20,23], or an alteration of primary microstructural and mechanical characteristics. Typically, the methods used to achieve inoculation are uncontrollable and rely on blowing powder into the melt pool or introducing a particle infused sticky residue pre-deposition to the previously deposited layer [20]. Refinement by alloy modification may occur via development of new wire compositions, however, this is expensive.

Ultrasonic agitation of the melt pool has demonstrated success in refining the columnar prior- β grain structure in powder processes. The vibration induces acoustic cavitation inside the melt pool, activating nucleation [24] and triggering dendrite fragmentation [25] leading to the development of an equiaxed grain structure, whereby newly formed nuclei and fragmented dendrites impede the growth of epitaxially grown grains and thus formation of a columnar prior- β grain structure. However, this method of refinement requires high frequency vibration. In powder processes or deposition of ‘small’ components this is feasible. For applicability to large-scale WAAM components that may weigh upwards of 10’s of kilograms, this method does not appear practically replicable and is yet to be demonstrated successfully.

Mechanical processing of WAAM components is currently the most feasible and widely researched method of grain structure control in titanium alloys. The introduction of a plastic strain to a deposit post-solidification provides β grains the opportunity to recrystallise upon the subsequent heating cycle of the successive layer being deposited. The most common methods for mechanical processing of titanium alloys are rolling [18] and machine hammer peening [21,26], with new processes such as in-situ ‘hot-forging’ being developed that may become applicable to titanium alloy systems [27,28]. The effectiveness of mechanical postprocessing on the prior- β grain structure is substantial, however, it also leads to an outer skin of non-refined grains with only the central bulk of material being refined, usually this is less prevalent with rolling than peening [19]. The major limitations of this method include the reduced complexity of deposition features to allow access for the rolling or peening tool to effectively refine the grain structure and the requirement of large-scale machinery for rolling. In both cases the additional post-processing leads to a reduction in productivity.

All described methods provide metallurgical and processing clues for the requirements of achieving refinement, i.e. constitutional supercooling and recrystallisation. However, translation into direct process control, i.e. a method based upon the manipulation of the process parameters, has demonstrated little success in refining the prior- β grain structure of Ti-6Al-4V in the as-deposited condition. The current refinement techniques add constraints on part design and freedom, incurring greater capital cost and lead time, and are counterproductive and contrary to the ethos of WAAM [2].

This paper demonstrates a new and novel approach to produce a refined prior- β grain structure and weakening of texture in the deposition of Ti-6Al-4V by WAAM and understanding of the α phase microstructural effects through prior- β grain structure control in the as-deposited condition, giving greater design flexibility and potential for localisation of grain structure (and by extension mechanical properties), without introducing further capital cost or lead time.

3.2 Theory

Classical solidification theory suggests that to achieve the columnar to equiaxed transition, i.e. grain refinement, it is essential for supercooled solute to exist ahead of the solidification front, to allow equiaxed grains to form via homogeneous nucleation and/or survival and growth of fragmented dendrites within the melt pool. Additionally, this requires either a reduction in the thermal gradient or an increase in the solidification velocity to promote nucleation [22,24,29–32]. The thermal gradient is responsible for defining the morphology of the solidification as either planar, cellular or dendritic dependent on its value [33]. During WAAM, a dendritic solidification front exists, where dendrites grow opposite to the heat flux, i.e. from the substrate into the melt pool [34]. The solidification velocity has an effect on the amount of constitutional supercooling at the solidification front, with an increase causing compression of the solute rejection and increased cooling rate, preventing a nucleus remelting thus increasing its survival rate [29].

An attempt to increase the solidification velocity by increasing the travel speed (TS) during deposition demonstrated that a mixed grain structure was obtainable [30]. The resulting prior- β grain structure comprised of distinctly columnar grains, however, a mixture of smaller and medium-sized refined grains proved obtainable along the columnar grain boundaries. Using a pyrometer to measure the melt pool temperature during deposition, Bermingham et al. [30] were able to retrospectively calculate a simplified thermal gradient, based upon a linear thermal gradient approximation and rectangular melt pool shape with the layer height and solidification temperature known. This enabled the prediction of grain structures in agreement with the solidification map presented by Kobryn and Semiatin [32]. The mixed grain structure should not have been unexpected due to the decrease in the wire feed speed/travel speed (WFS/TS) ratio as TS

increased. It has been demonstrated elsewhere that a decrease in the WFS/TS ratio reduces the layer height [35]. Therefore, increasing the solidification velocity by means of the travel speed was not efficient at refining grain structure as this incurred an increase in the thermal gradient during solidification, hence the mixed grain structure.

Resistive heating of the feedstock wire to enable a reduction in the arc current has been shown to successfully refine prior- β grains [36]. The underlying mechanism was attributed to a reduction in the thermal gradient that was obtained in the melt pool as the arc heat input was reduced with increasing resistive heating current. The methodology required the feedstock to be fed directly into the melt pool to complete a resistive heating circuit, the larger the resistive current the lower the arc current required. It can be observed that the overall energy input to the deposit was decreasing as there was a notable decrease in width and increase in layer height. Using the simplified method detailed by Bermingham et al. [30], a reduction in thermal gradient would be observed and at face-value the reason for refinement. However, by penetrating the melt pool with the feedstock there would be significant melt pool agitation and the introduction of a negative thermal gradient at the contact point (where the temperature of the un-melted wire is lower than the melt pool temperature) and likely dendritic fragmentation. Therefore, the mechanism of refinement cannot be explicitly determined. Additionally, innate process fluctuations, in order to maintain continuous penetration of the melt pool, is difficult and considered unstable by Rios et al. [37] with the possibility for numerous process defects including lack of fusion, spatter and misalignment of the wire feedstock.

A study by Wang et al. [38] demonstrated the ability to deposit a localised grain structure. Through the variation of WFS for a fixed heat input, a columnar to fully equiaxed specimen was deposited. The mechanism behind the refinement is still unclear. It was surmised that there was a reduction in the thermal gradient as the increased volume of wire cooled the melt pool and similarly relied on the wire entering the melt pool to generate a negative thermal gradient to block epitaxial growth. This appeared in a similar study by Wang et al. [39] which demonstrated the same level of refinement through deliberately forcing the feedstock to penetrate the melt pool. Wang et al. [39] argued that a localised negative thermal gradient acts as a nucleation front at the top of the melt pool, with additional agitation to activate nucleation and dendrite fragmentation also responsible. However, reliance on this process condition does not provide a stable process

and is not applicable in all methods of deposition, and ultimately this type of transfer mode is generally avoided as it can lead to numerous potential defects [37].

Whilst these studies have shown evidence of success, questions remain on the mechanisms of refinement and their reliability. Studies that show refinement without a reliance on melt pool agitation were unable to deposit a fully refined structure, although previous studies indicate that the total energy supplied during deposition influences the grain structure achieved. Hence, to deposit a refined prior- β grain structure in Ti-6Al-4V via control of processing conditions, whilst maintaining a stable process condition without melt pool agitation, a new parameter, the specific energy density of deposited material (SED), detailed in Equation 3-1, is proposed.

$$SED (J.mm^{-3}) = \frac{4\eta_A VI}{WFS \cdot \pi d^2} \dots \dots (3-1)$$

Equation 3-1 compiles the basic deposition parameters (where η_A represents the process efficiency taken from BS EN 1011-1:2009 for plasma arc welding, V and I represent arc voltage and current, WFS , the wire feed speed and d the wire feedstock diameter) and can be easily manipulated via the WFS. The expected outcome was that as SED reduced, the total energy would be shared across a larger volume of deposited material, reducing the overall melt pool temperature and thus thermal gradient. A significant reduction in the thermal gradient would drive homogenous nucleation and trigger grain refinement. The SED represents the total energy delivered to and shared by the feedstock material and is not to be confused with the heat input (HI), which measures the total energy delivered to the substrate. In this study the total heat input, measured by Equation 3-2 (where TS represents the travel speed of the torch), did not change as the arc energy and travel speed remained constant.

$$HI (J.mm^{-1}) = \frac{\eta_A VI}{TS} \dots \dots (3-2)$$

3.3 Methodology

In this study a total of five samples were deposited on individual Ti-6Al-4V substrates (175 mm x 50 mm x 10 mm) clamped to an aluminium backing plate at all four corners. A PWP Viper MC plasma torch was coupled to a TECARC PLASWELD 400 DC power source and used to deposit 150 mm long deposits. Two Migatron KT4 wire feeders were

front-fed into the centre of the arc, at identical WFS, to feed 1.2 mm diameter Ti-6Al-4V wire feedstock with a 10° offset. All samples were deposited inside a globally shielded environment purged with UN1006 Pureshield Argon to maintain an oxygen level of < 100 PPM monitored by a Argweld PurgEye 600. A schematic of the experimental setup is illustrated in Figure 3-1. The wire feedstock composition is provided by the manufacturer (Perryman) subject to their quality assurance methods at the time of production in Table 3-1.

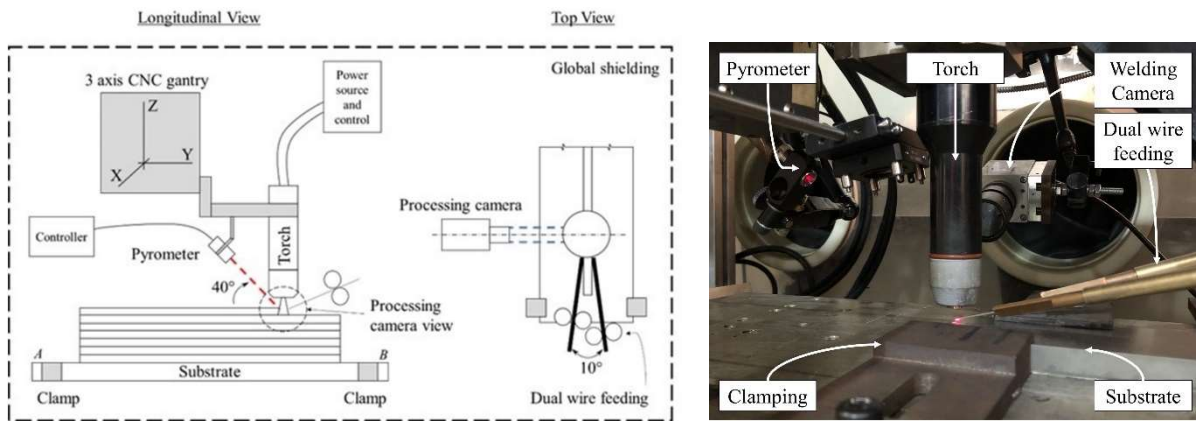


Figure 3-1: (L) Schematic of experimental setup. (R) Experimental setup.

Table 3-1: Wire feedstock composition Ti-6Al-4V (wt %)

O	N	C	Fe	Al	V	Si	H	Ti
0.15	0.008	0.021	0.18	6.14	3.94	0.012	0.0004	BAL

A single pass, single direction deposition strategy was utilised, controlled via a CNC gantry. In all cases a minimum of 20 mm was first deposited to account for conduction losses through the substrate. This effect is present during the initial layers of a deposit due to the high heat extraction rate from the substrate material, drawing heat away by conduction and is indicated by the stability of the bead geometry in terms of width and height. A further 30 mm of material was deposited for microstructural analysis. During deposition all layers were cooled to < 40°C aided by a cooling line containing UN1006 Pureshield Argon after a single minute of ambient cooling. This removed variability in pre-deposition temperature as the thermal mass changed with the addition of each deposited layer, a pre-defined cooling time would not account for this and would lead to inconsistency between the deposition start and end point.

All processing parameters were kept constant with the exception of combined WFS, manipulated to achieve the desired SED. The WFS's chosen for this study were determined by the SED calculated from the study by Wang et al. [38]. Table 3-2 indicates the parameters used in this study.

Table 3-2: Deposition parameters

ID	Voltage (V)	Current (A)	Travel Speed (mm.s ⁻¹)	Total WFS (mm.s ⁻¹)	SED (J. mm ⁻³)
1	18.41	103.57	4.00	26.67	37.93
2	18.74	103.52	4.00	33.87	30.39
3	19.07	103.21	4.00	36.67	28.48
4	18.79	104.29	4.00	46.67	22.28
5	19.81	102.95	4.00	50.00	21.64

A Sensortherm Metis M311 2-colour pyrometer was used to measure the melt pool temperature with the spot centre 2 mm behind the arc centre at an angle of 40° from the substrate at a focal length of 120 mm and 15 ms response time. This point was selected as the closest point to the centre of the melt pool (where the melt pool temperature is hottest) within the physical limitations of the setup, and culminated in an ovular spot size of 2.2 mm x 1.6 mm. The thermal gradient of all samples was calculated using the simplified method outlined by Bermingham et al. [30]. An emissivity value of 0.36 was extrapolated from existing literature for liquid titanium [40]. The average melt pool temperature measured was used for the calculation and error calculated considering standard error [41] and instrumentation error of 0.3% as specified by the manufacturer throughout.

Deposition was monitored using a Xiris XVC-1100 welding process camera to ensure process stability and a consistent ‘droplet’ feedstock transfer mode. To ensure high image quality the camera aperture was decreased to the manufacturer’s minimum and a rolling shutter mode with 10µs exposure time selected. A Xiris 50 mm lens was used in conjunction with a Xiris UV filter and clear glass spatter protection window.

Two specimens were machined from the centre of each deposit for metallurgical analysis. A 30 mm x 30 mm transverse longitudinal section, machined to the central plane and a transverse section to look at the cross-section of the deposit. All samples were mounted in conductive phenolic resin using a hot mounting press and mechanically polished using

consecutive grades of SiC paper from 240 grit to 2000 grit, before a final polish using colloidal silica and oxalic acid and etched using Kroll's reagent for approximately 10 seconds. Electron backscatter diffraction (EBSD) analysis was conducted using a Thermo Scientific Apreo C FEG-SEM at 20 kv accelerating voltage and 51 nA beam current with 15 μm step size and processed using Oxford Instruments AztecCrystal. As Ti-6Al-4V exhibits allotropic behaviour, a solid state β to α transformation occurs during cooling, therefore, the β phase cannot be directly observed at room temperature. The transformation follows Burger's orientation relationship (BOR) i.e. $\{110\}_{\beta} // \{0001\}_{\alpha}$ and $\langle 111 \rangle_{\beta} // \langle 0001 \rangle_{\alpha}$ [42], which allows prior- β -phase maps to be generated from the acquired room temperature α -phase data using parent grain reconstruction developed by Davies and Wynne [43,44], with up to 3° divergence from BOR considered as part of the same grain and up to a 2° misorientation from a particular variant accepted. Quantitative prior- β grain size data was captured automatically by Oxford Instruments Aztec Crystal software and reported using the equivalent circle diameter, with grains < 200 μm being excluded to account for reconstruction errors. A high resolution large area mapping Hirox RH-2000 microscope was used for optical microscopy at 50x magnification.

Microhardness measurements were conducted using a Innovatest Falcon 503 and Vickers hardness test. A 300 g load was selected with an indentation dwell time of 10 seconds and 0.5 mm spacing from the manufacturer's recommendation. A total of 48 measurements were taken along the central plane from the top to bottom of the longitudinal specimens post-polishing and EBSD data acquisition.

3.4. Results and Discussion

The macrographs of the five longitudinal specimens may be observed in Figure 3-2. There is a clear morphological change in the as-deposited prior- β grain structure. Figure 3-2a) demonstrates a typical columnar grain structure, with the prior- β grains extending from the bottom of the deposit to the top. Moving through Figures 3-2b) and 3-2c) the columnar grain structure begins to break down and refined grains begin to appear at the grain boundaries. Figures 3-2 d) and e) show a fully refined prior- β grain structure comprised of smaller refined grains. Evident in the macrographs presented in Figure 3-2, is the effect of the thermal cycling innate to the WAAM process. This is demonstrated by the evidence of microstructural banding that is caused by the reheating of previously deposited material

during subsequent deposition up to the β -transus temperature. The white banding appears as the α lamellar are coarsening [12] as they are essentially heat-treated close to the β transus and continue to grow. As the SED is reduced, the accompanying increase in layer height means the spacing between banding is becoming greater and less bands are visible in the specimens, improving homogeneity.

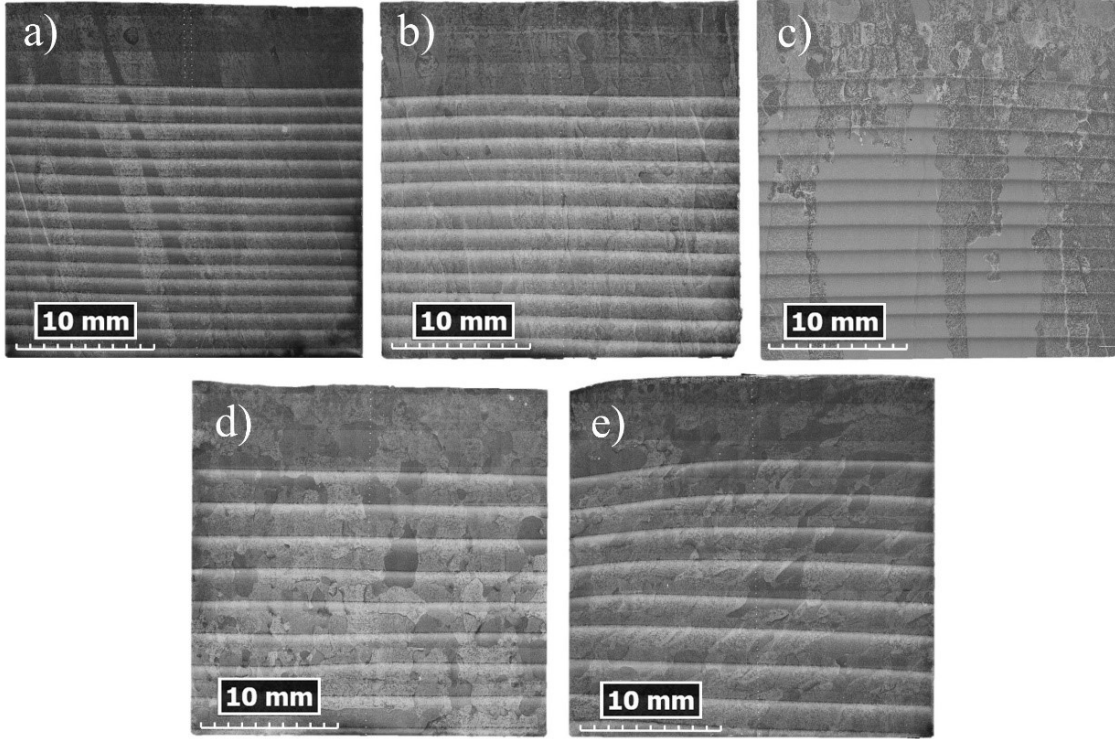


Figure 3-2: Light macrographs of etched longitudinal specimens of Ti-6Al-4V specimens 1 – 5 illustrating change in prior- β grain morphology changes as SED of deposited material is reduced a) $37.93 \text{ J} \cdot \text{mm}^{-3}$, b) $30.39 \text{ J} \cdot \text{mm}^{-3}$, c) $28.48 \text{ J} \cdot \text{mm}^{-3}$, d) $22.28 \text{ J} \cdot \text{mm}^{-3}$, e) $21.64 \text{ J} \cdot \text{mm}^{-3}$.

The columnar grain structure is caused by a combination of the high thermal gradient present during solidification and minimal solute segregation, minimising the amount of potential constitutional supercooling [22]. Aluminium and vanadium do not segregate sufficiently in titanium to generate a large liquidus temperature (T_L) difference close to the solidification front. Reported partition coefficients for aluminium and vanadium range from 1.01 – 1.13 and 0.89 – 0.96 respectively [45,46]. With partition coefficients close to unity a significant change in thermal gradient is required to generate any constitutional supercooling. Typically, the WAAM process exhibits high thermal gradients making constitutional supercooling difficult to achieve in the as-deposited condition which prevents homogenous nucleation or survival rate ahead of the solidification front, as is the case for the initial specimens. Growth occurred via an epitaxial growth mechanism, where solidifying atoms readily attach themselves to the pre-existing partially melted

lattice of the previous grain, as this requires substantially less free energy than homogenous nucleation [47]. The resultant effect is the continuation of the previously deposited grain (columnar) in the same crystallographic orientation (texture). With the reduction in SED a morphological change in prior- β grain structure may be observed. As the arc energy, travel speed and alloy composition remain constant, this indicates that it is a response to a reduction in the thermal gradient. A reduction in the thermal gradient generates constitutional supercooling, illustrated diagrammatically in Figure 3-3, (note that for Ti-6Al-4V there is only a small change in T_L due to minimal solute partitioning and has been inflated diagrammatically for the purpose of explanation). Additionally, this highlights the difficulty in achieving prior- β grain refinement for Ti-6Al-4V, as the process window is minimal and difficult to obtain. The reduction in SED, thus thermal gradient, allows potential for nucleation ahead of the solidification front in the melt pool, increasing the survivability of randomly orientated dendrites and/or dendrite fragments from remelting and encouraging the potential for nucleation [29]. These factors combined increase the opportunity for competitive growth and disruption to the epitaxial columnar grain structure, refining prior- β grain morphology and weakening of texture.

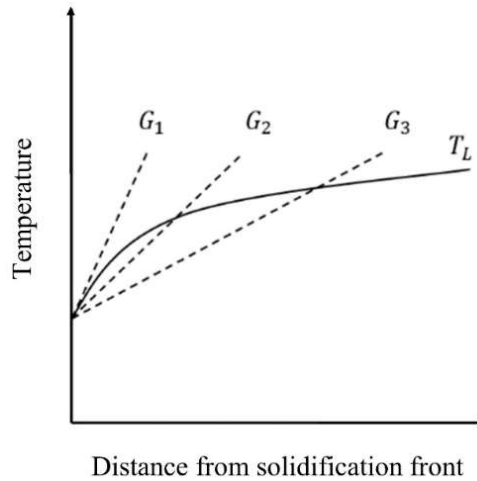


Figure 3-3: Illustration outlining the effect of how a reduction in thermal gradient increases the total amount of constitutional supercooling by increasing the total area created by the liquidus temperature line (T_L) and dashed thermal gradient line. Note that the curvature of T_L does not represent Ti-6Al-4V and is inflated for the purpose of explanation.

Thermal gradients were calculated for each specimen using the simplified method outlined by Bermingham et al. [30]. This method required taking the difference between the peak temperature of the melt pool during deposition and solidification temperature and dividing over the height of the melt pool, thus providing an average linear thermal gradient approximation. These were determined to be: $528.4 \pm 34.8^\circ\text{C}.\text{mm}^{-1}$, $351.1 \pm$

24.7°C.mm⁻¹, 283.5 ± 43.7°C.mm⁻¹, 208.0 ± 26.7°C.mm⁻¹ and 196.6 ± 27.1°C.mm⁻¹ for specimens 1 – 5 respectively. It can be deduced mathematically that the dominant variable for the calculation is the layer height during deposition. As may be observed in Figure 3-4, the average layer height increased from 1.14 mm in specimen 1 to 2.48 mm in specimen 5, whilst the average peak temperature during deposition reduced from 2250°C to 2130°C. The average measured peak temperature remains consistent across specimens 1 – 2 and specimens 3 – 5, with an average temperature drop of ~ 100°C occurring at specimen 3, which has a negligible effect on the thermal gradient calculated. Thus, the assumption that a reduction in SED would cool the melt pool is not unfounded but was not directly responsible for the drop in temperature as demonstrated by specimens 3 – 5, that have equivalent melt pool temperatures, instead it occurs in relation to the feedstock wire transfer mode.

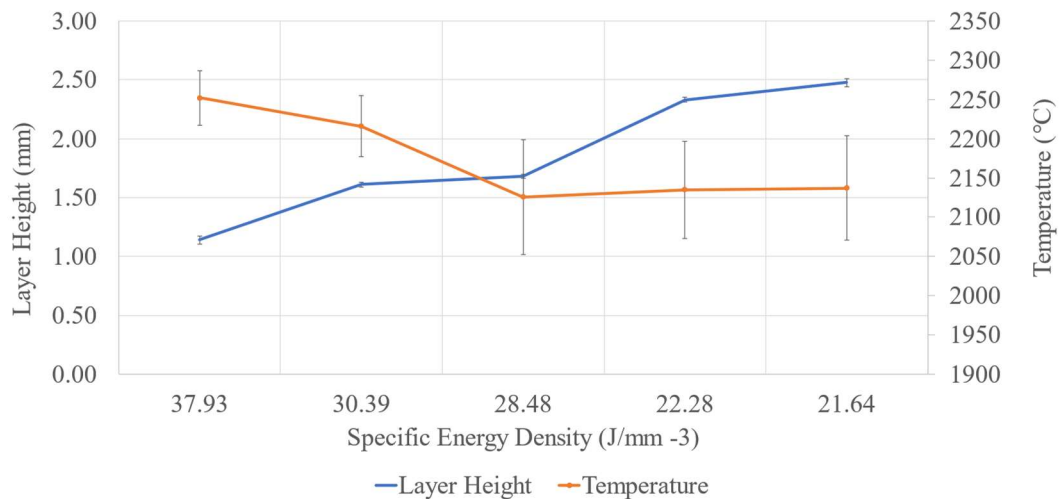


Figure 3-4: Effect of SED on layer height and recorded temperature during deposition. (Specimen 1 – 5 reading left to right).

As the SED was reduced there was a noticeable difference in the transfer mode (TM) of the feedstock material to the substrate from a small droplet to a large droplet. As described by Rios et. al. [37] the transfer mode during plasma arc welding with wire feedstock is categorised into four basic transfer modes: transfer mode 1 (TM1) the feedstock is in permanent contact with the melt pool with no interruptions; transfer mode 2 (TM2) is a droplet transfer mode where the droplet contact with the melt pool is approximately equivalent to the time required to grow a new droplet; transfer mode 3 (TM3) the growth time of the droplet is larger than the contact time and transfer mode 4 (TM4) growth time is significantly larger than the contact time and is reliant on the arc pressure to shear the

droplet from the wire leading to erratic free fall. TM3 has a high potential to transform to TM4 and may be observed by the formation of spatter alongside the WAAM deposit. Generally, for stable deposition it is preferable that TM2 is maintained as it provides no risk of erratic droplet placement and a consistent frequency of droplet thus deposit shape. Transfer mode can be controlled via the wire positioning within the arc and optimisation of deposition rate. During TM1, insufficiently melted feedstock has the possibility to fully penetrate the melt pool and skitter at the bottom of the melt pool leading to potential defects such as lack of fusion. TM4 should be avoided due to its erratic and unstable nature. Whilst TM3 is not ideal, in the case of this study no spatter was formed and droplet transfer and bead shape remained consistent when monitored via the processing camera. Therefore, in this controlled experimental environment both TM2 and TM3 can be referred to as stable.

The effects of feedstock TM on the heat flow and bead shape have been investigated extensively by Chen et. al. [48] and can be used to understand the reduction in peak temperature observed. A change in transfer mode was observed with the reduction in SED, from the two feed wires melting individually by small droplets (TM2) in specimens 1 and 2, before merging to create a singular larger droplet (TM3) in specimens 3 – 5. This may be observed in Figure 3-5 for specimens 1 – 5 at the same randomly selected build height (~ 38 mm). It is important to note that whilst the larger droplet forms, the ‘cold’ wire does not penetrate the melt pool and a droplet transfer mode was maintained. Therefore, no benefits of melt pool agitation or introduction of negative thermal gradients to influence the grain structure was provided. The ~ 100°C drop was a consequence of the arc shading of the melt pool due to a reduction in the interaction between the arc and substrate caused by the larger droplet. The indication being that a reduction in the SED was not affecting the peak temperature observed during deposition. A similar effect is reported by Wang et al. [49], where the influence of wire diameter and deposition rate was considered. They demonstrated a large diameter wire (causing greater shading) led to less energy being delivered to the melt pool, measurable by the change in bead geometry in comparison to an equivalent deposition rate of a smaller diameter wire [49].

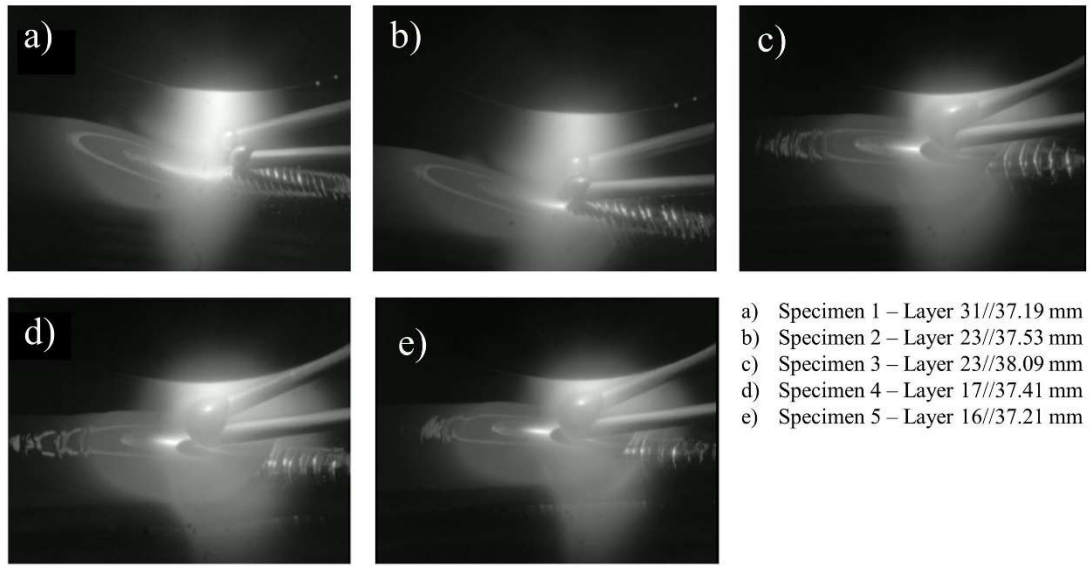


Figure 3-5: Droplet transfer mode during deposition. a) $37.93 \text{ J} \cdot \text{mm}^{-3}$ – TM2, b) $30.39 \text{ J} \cdot \text{mm}^{-3}$ – TM2, c) $28.48 \text{ J} \cdot \text{mm}^{-3}$ – TM3, d) $22.28 \text{ J} \cdot \text{mm}^{-3}$ – TM3, e) $21.64 \text{ J} \cdot \text{mm}^{-3}$ – TM3 at $\sim 38 \text{ mm}$ build height.

Additionally, it may be observed that the increase in average peak temperature uncertainty for specimens 3 – 5 was comparatively larger than specimens 1 and 2, which may also be attributed to the change in transfer mode and arc shading. The real-time pyrometric measurements recorded during deposition of specimens 1 – 5 for the respective layers observed in Figure 3-5 is illustrated in Figure 3-6. During TM2 for specimens 1 and 2 it may be observed that the variation in temperature was smaller than TM3. This can be attributed to the aforementioned change in arc interaction with the melt pool due to arc shading. Whilst the droplet was growing larger during TM3 than TM2, this allowed additional time for the melt pool to cool and prevented an equivalent amount of arc energy to interact with the melt pool surface, reducing the peak temperature. The point at which the droplet detached, the arc was fully interacting with the melt pool at an equivalent rate to TM2 and heating the melt pool surface. Once the TM3 droplet size grew beyond the TM2 droplet detachment size, the melt pool began to cool at a faster rate once more. Taking into account the temperature peaks, it is possible to calculate the frequency of droplet transfer if necessary.

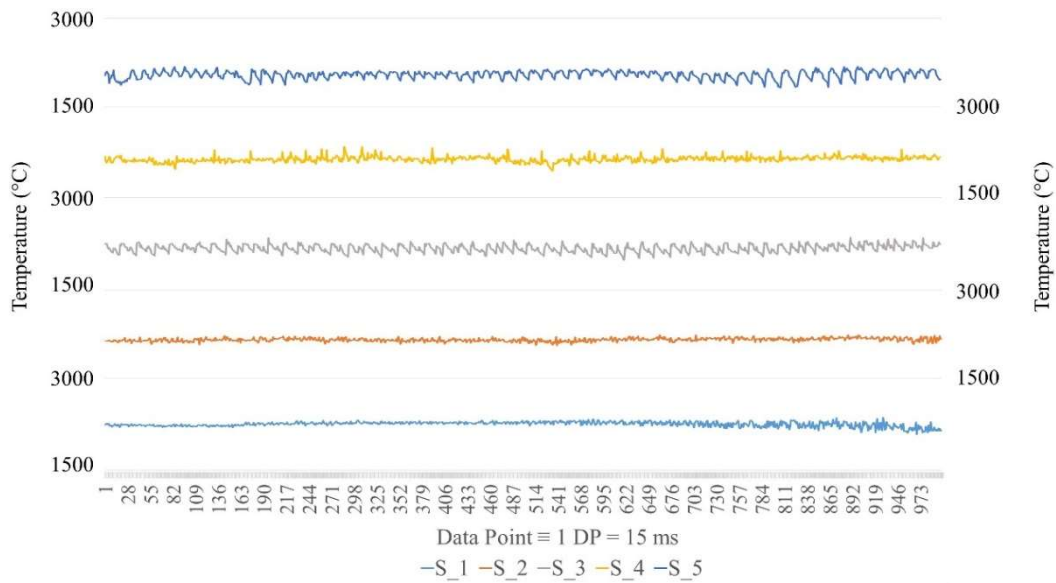


Figure 3-6: Real-time pyrometric recording for specimens 1 – 5 (ascending). (15 ms interval time per data point.) Specimen layers: 31, 23, 23, 17, 16 with respect to Figure 3-5 observed transfer modes.

EBSD prior- β phase reconstructed maps of the five specimens may be observed in Figure 3-7. Analysis of specimen 1 (Figure 3-7a) highlights the texture of the columnar grain structure with weak misorientations of $< 5^\circ$ indicated by the similar shade of inverse pole figure (IPF) colouring with respect to the build direction. In this thermally stabilised region of material, heat primarily flows downwards by conduction and alongside the epitaxial growth mechanism, the grains have orientated themselves in to the ‘easy’ growth direction close to the build direction (BD), $<100>_\beta$ in the case of BCC β -phase titanium. As the SED reduces, specimens 2 and 3 (Figure 3-7b and 3-7c) show evidence of the columnar structure beginning to break down with the introduction of randomly orientated refined grains appearing along the columnar grain boundaries. The texture was largely evident in the remaining columnar grains but shows evidence of weakening with the presence of high angle grain boundaries, indicated by the different (non-red) IPF colouring with respect to the build direction. In specimens 4 and 5 (Figure 3-7d and 3-7e) a complete breakdown of the columnar structure to a refined one is indicated by the randomness of the IPF colouring and shape of the grains that may be observed. This is where grains have been prevented to grow via an epitaxial growth mechanism and instead are seemingly homogeneously nucleated and grow competitively in randomly orientated directions.

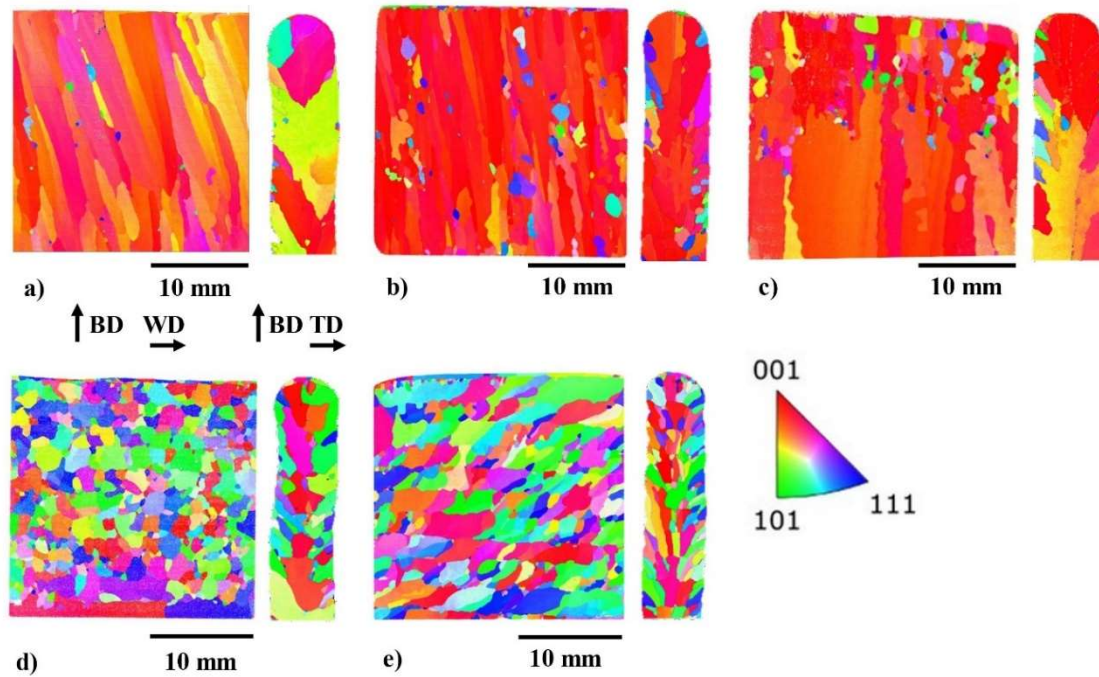


Figure 3-7: EBSD IPF maps of Ti-6Al-4V specimens 1 – 5 with reducing SED, a) $37.93 \text{ J} \cdot \text{mm}^{-3}$, b) $30.39 \text{ J} \cdot \text{mm}^{-3}$, c) $28.48 \text{ J} \cdot \text{mm}^{-3}$, d) $22.28 \text{ J} \cdot \text{mm}^{-3}$ e) $21.64 \text{ J} \cdot \text{mm}^{-3}$, showing the transition from a columnar grain structure to a refined one in both the longitudinal and transverse plane.

The breakdown of texture as the SED reduces may be observed via the pole figures in Figure 3-8. In specimen 1 and 2 (Figure 3-8a and 3-8b) a distinctive concentration can be observed with a highly textured $\langle 100 \rangle_{\beta}$ growth direction closest to the build direction. This was not unexpected due to the epitaxial growth mechanism that dominates solidification. In specimen 3 (Figure 3-8c), this texture begins to break down as grains are no longer solely developed by epitaxial growth but grow by new randomly orientated nucleation as well. In specimen 4 (Figure 3-8d), it may be observed that the texture is no longer present with no distinctive areas of concentration. The implication being that at a reduced SED value it is possible to remove both the columnar prior- β grains and the crystallographic texture to produce grains via seemingly homogenous nucleation and competitive growth. In specimen 5 (Figure 3-8e), qualitative examination of the prior- β grain reconstruction maps highlights a shift from the random orientation of the grains in specimen 4, implying there is an optimal value for SED to achieve refinement, to tilting towards the direction of the heat source travel direction. This is confirmed in the pole figure, with two concentrations appearing, tilted away from the BD to the working (WD) and transverse directions (TD). This appears to be evidence of the growth mechanism returning to an uncompetitive state, not unlike the typical columnar grain structure, albeit

in the horizontal direction. It is known that preferential grain growth occurs along the maximum thermal gradient perpendicular to the solidification front [22,30]. As the SED reduced, the layer height increased, therefore the melt pool shape is evolving with solidification first occurring at the rear of the melt pool seemingly providing a growth advantage. It is therefore implied that the melt pool shape may also play an important role in determining prior- β grain morphology and texture, therefore, this mechanism requires further investigation.

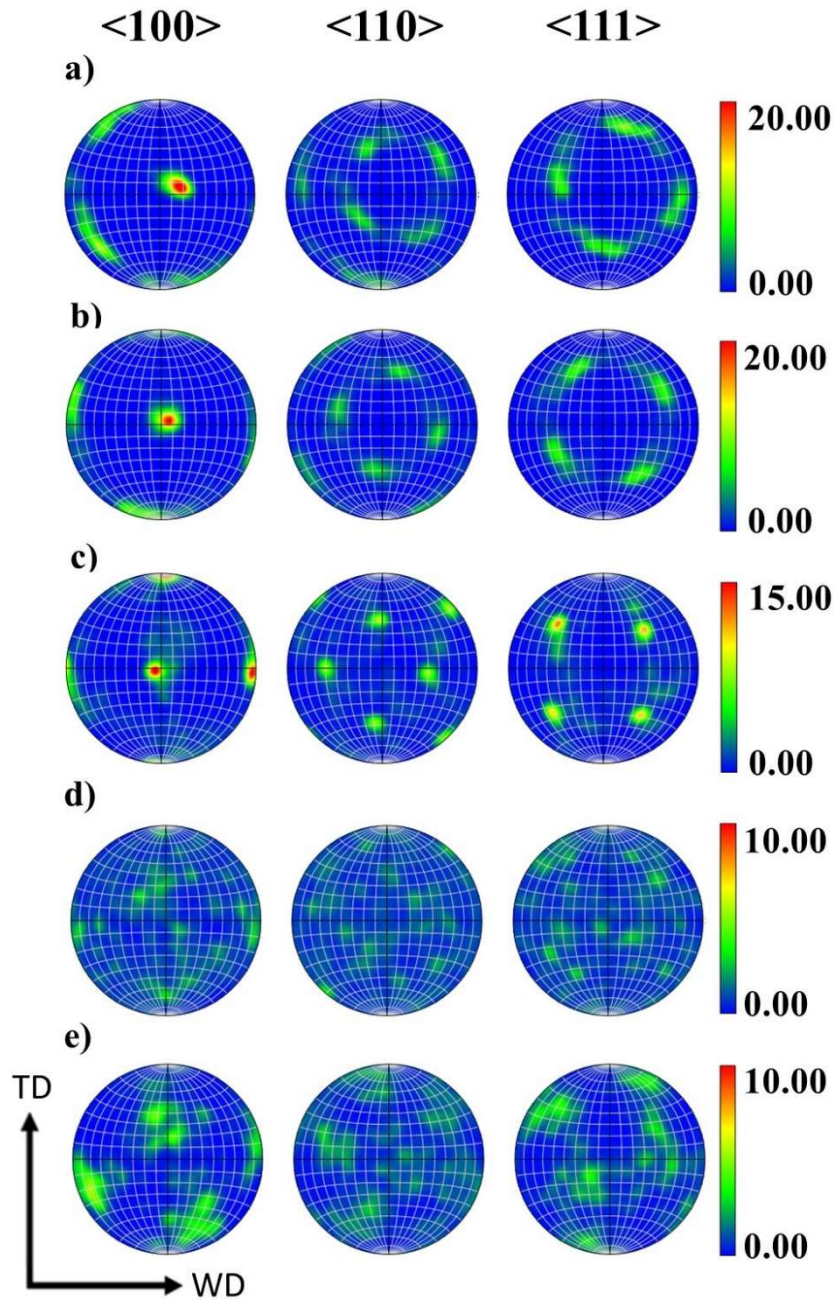


Figure 3-8: Pole figures of Ti-6Al-4V specimens 1 – 5 indicating crystallographic texture a) $37.93 \text{ J} \cdot \text{mm}^{-3}$ b) $30.39 \text{ J} \cdot \text{mm}^{-3}$, c) $28.48 \text{ J} \cdot \text{mm}^{-3}$, d) $22.28 \text{ J} \cdot \text{mm}^{-3}$, e) $21.64 \text{ J} \cdot \text{mm}^{-3}$.

It is possible to consider the misorientation relationships between the prior- β grains to give an indication of whether solidification by nucleation ahead of the solidification front occurred. Should free homogenous nucleation occur, prior- β grains would demonstrate a random misorientation distribution that can be described by the well-known Mackenzie distribution for cubic materials [50,51]. Consideration of the prior- β grain boundary misorientation evolution may be observed in Figure 3-9. It is clear that for specimen 1, where the SED is highest (37.93 J.mm^{-3}), the grain boundary misorientations are dominated by low angle grain boundaries (LAGB) $< 10^\circ$. As the SED was decreased, a shift towards the Mackenzie distribution took place with fewer LAGB present. At the point of optimal prior- β grain refinement in specimen 4 (22.28 J.mm^{-3}), the misorientations show propensity to the Mackenzie distribution inferring nucleation ahead of the solidification front. As the SED was decreased to its minimum in specimen 5 (21.64 J.mm^{-3}) and the horizontally tilted prior- β grains manifest, the misorientations show propensity towards the Mackenzie distribution [50,51], but not as strongly as specimen 4. Interestingly, present in all specimens where some level of refinement has occurred, i.e. specimen 3 – 5, a strong 60° misorientation peak and to a lesser extent 51° peak manifests, indicating a further potential influence of the SED reduction on the prior- β grain structure. This may also be linked to the melt pool shape as previously discussed. Further investigation of this mechanism is required to fully understand its effects and its origin.

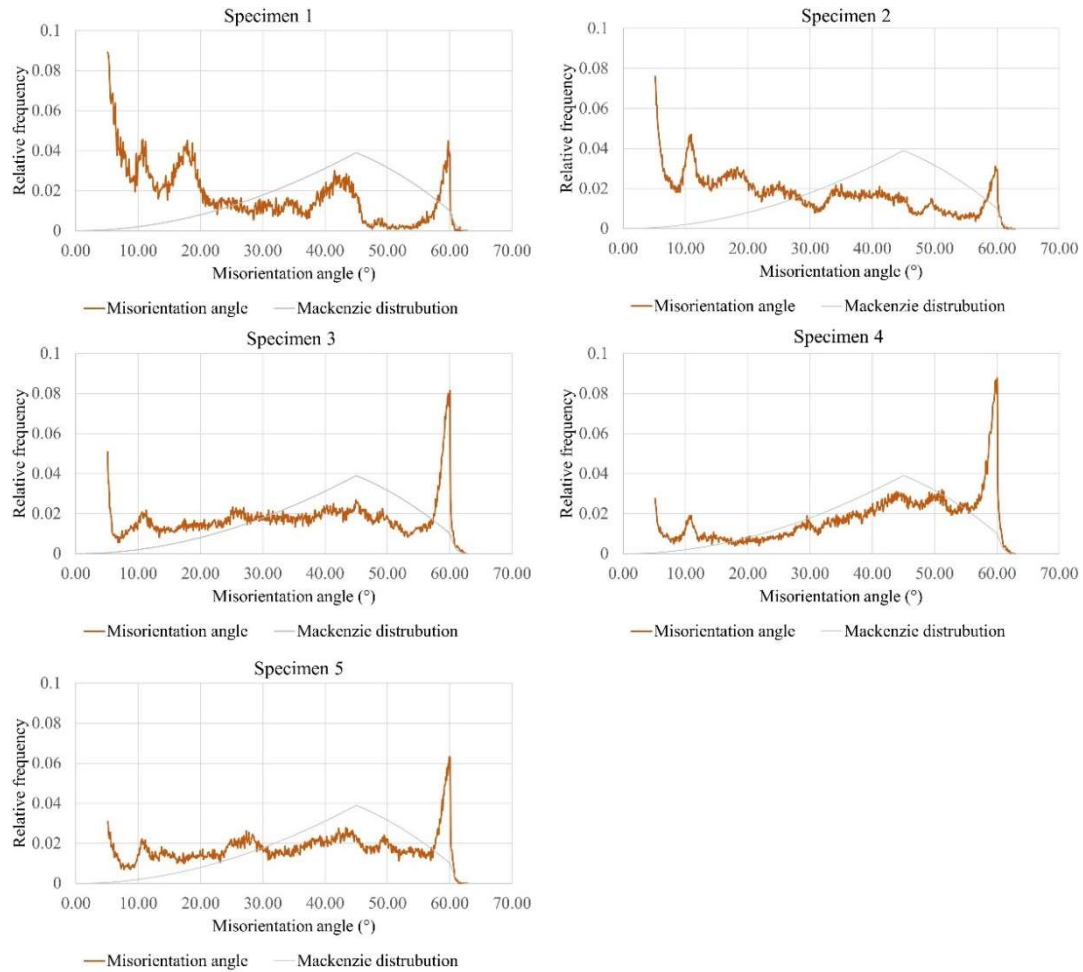


Figure 3-9: Prior- β grain boundary misorientations overlaying the Mackenzie distribution of specimens 1 – 5 [50,51].

Post prior- β reconstruction, the grain size in each specimen was measured according to the equivalent circle diameter, and the grain aspect ratio characterised to determine how close to an equiaxed structure was obtained during refinement (Table 3-3). However, given that the number of grains present in each specimen was relatively small, it is recommended that these results are indicative of the grain size and the grain size distribution should be consulted as reported in Figure 3-10.

Table 3-3: Effect of SED on average grain size and aspect ratio

Specimen	SED ($\text{J}\cdot\text{mm}^{-3}$)	Number of grains	Mean grain size (μm)	Mean aspect ratio
1	37.93	96	1797 ± 220	3.94 ± 0.26
2	30.39	313	1147 ± 64	3.69 ± 0.16
3	28.48	444	942 ± 46	2.33 ± 0.07
4	22.28	710	821 ± 23	1.83 ± 0.03
5	21.64	532	973 ± 34	2.47 ± 0.07

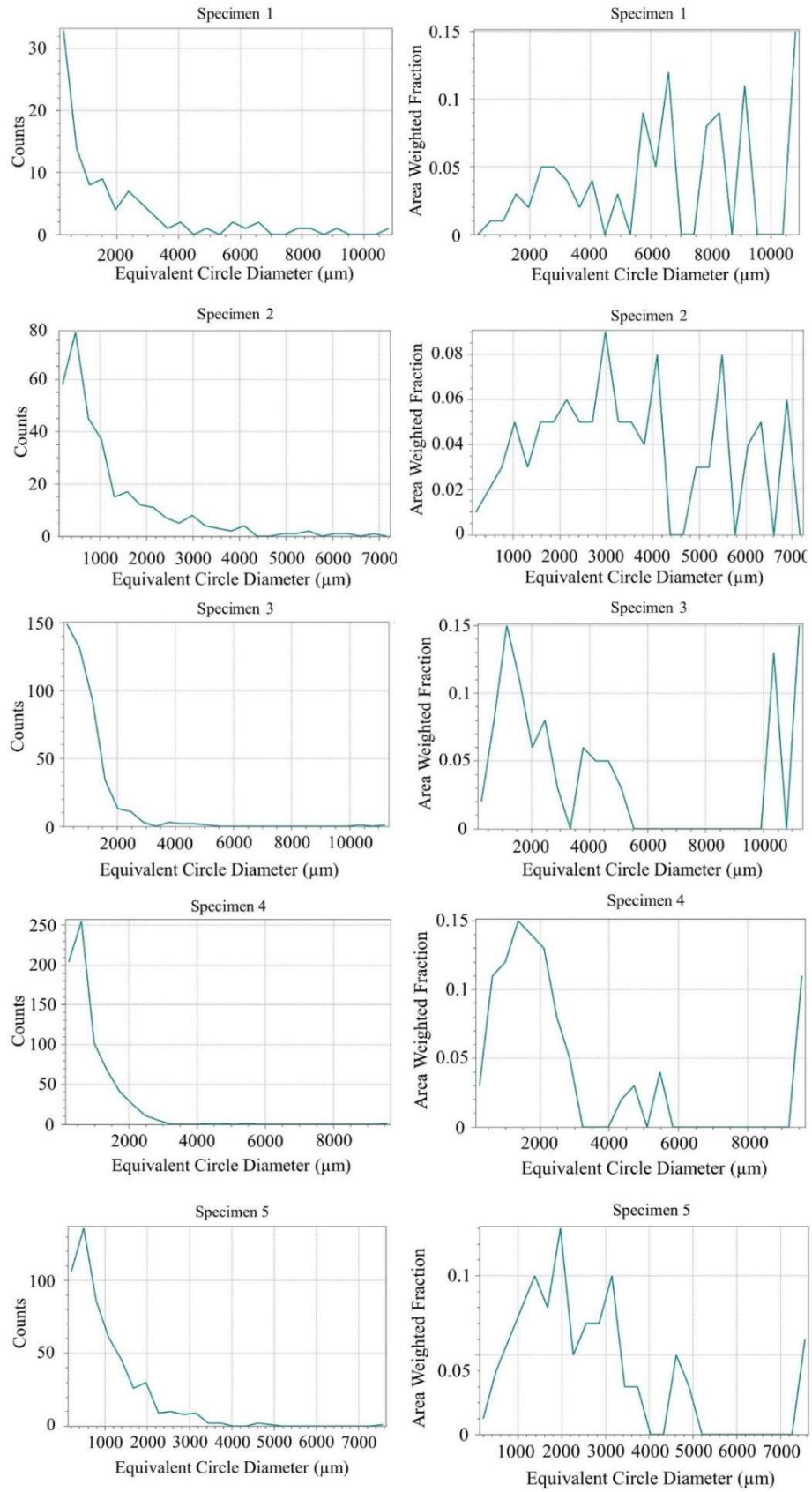


Figure 3-10: Grain size distribution of specimens 1 – 5. (L) Number of counted grains (R) Area weighted distribution of grain size.

As expected when SED was reduced, it may be observed that the total number of grains increased and their size reduced in specimens 1-4, however, an unexpected decrease in the number of grains and increase in size was observed in specimen 5. This is particularly prevalent in the area weighted fraction of the grain size. In specimen 1, grains $> 5000 \mu\text{m}$ dominated a large proportion of the grain structure. As the SED was reduced it may be observed that smaller grains accounted for an increasingly larger proportion of the measured area and by specimen 4 grains $< 2000 \mu\text{m}$ dominated. However, during the deposition of specimen 5, there was an increase in grain size with a larger proportion of grains growing between $2000 - 4000 \mu\text{m}$ despite a lower SED, which is likely in relation to the horizontal tilt and return of seemingly preferential growth.

Similarly, as may be observed in Figure 3-11, the aspect ratio decreased from specimens 1 – 4 until specimen 5 where an increase was also noted. In specimens 1 and 2, the aspect ratio of the grain was dominated by large > 3.0 aspect ratio grains. However, as refinement of the prior- β grains occurred the aspect ratio became dominated by ~ 2.0 aspect ratio grains in specimen 3 and ~ 1.5 in specimen 4, where optimal refinement occurred. Therefore, whilst grains have been significantly refined, there was some element of columnar structure retained. In specimen 5 as prior- β grains began to tilt horizontally, the aspect ratio slightly increased to be dominated by ~ 2.5 aspect ratio grains.

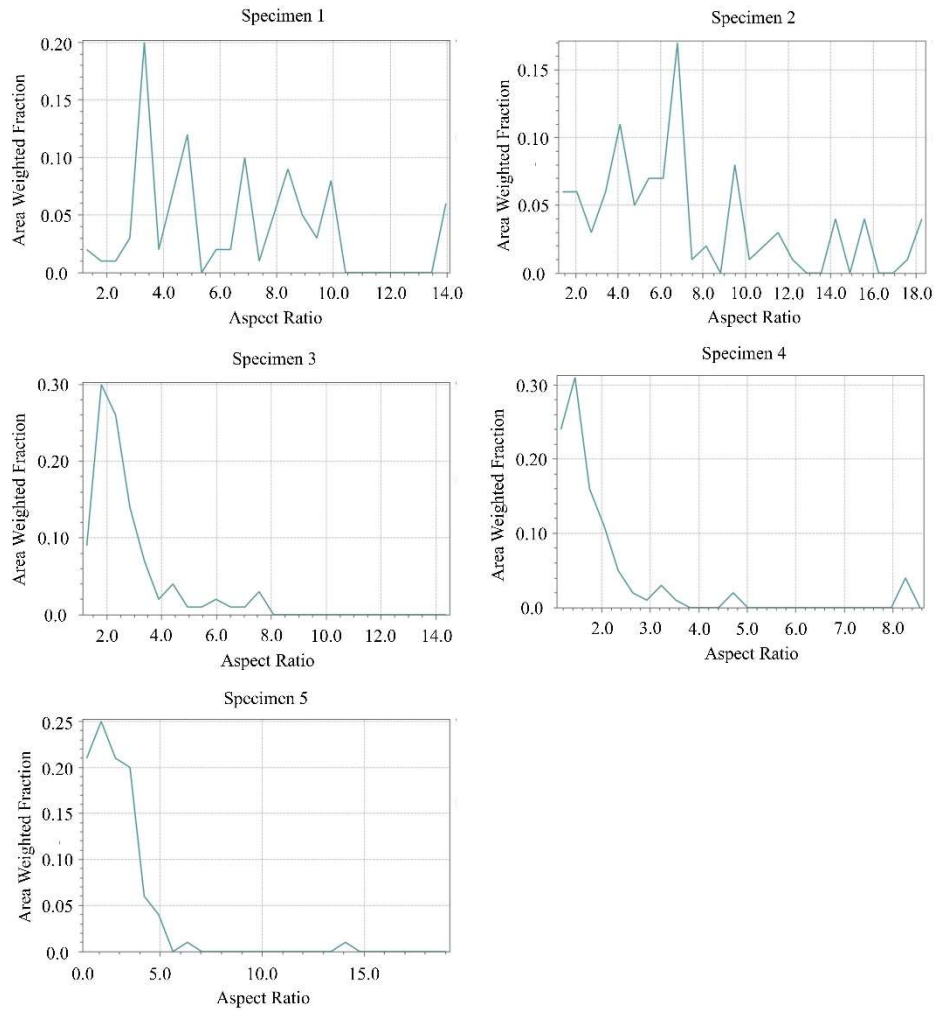


Figure 3-11: Aspect ratio distribution of specimens 1 – 5 as a function of area weighted fraction.

Figure 3-12 presents the α microstructure as viewed from the top of the specimen and bulk material. The α microstructures observed showed a predominantly Widmanstätten morphology where α plates overlap to create a basketweave effect. There is evidence of colony α , where several laths are grouped together in the same orientation and both elongated and fragmented α . Widmanstätten α is the most common microstructure observed in Ti-6Al-4V deposited with WAAM and is determined by the cooling rate during solidification [22,30,32]. It may be observed that the reduction in the SED from specimens 1, 4 and 5, where refined prior- β grains exist, had no effect on the size (as calculated using the automated method by Zhao et al. [52]) of the α lamellar and thus indicated no change in cooling rate as expected, as the heat input had remained constant with little change in peak melt pool temperature being measured. There was an increase in the inter-lamellar spacing (ILS) of the bulk material as compared to the top material of the specimen, due to the coarsening effect previously mentioned, as a result of innate

thermal cycling during WAAM heat treating the material. A smaller difference in the wall top and bulk ILS of specimens 4 and 5 may be observed compared to specimen 1 due to the reduction in the number of bands as a consequence of less thermal cycles spaced at larger intervals.

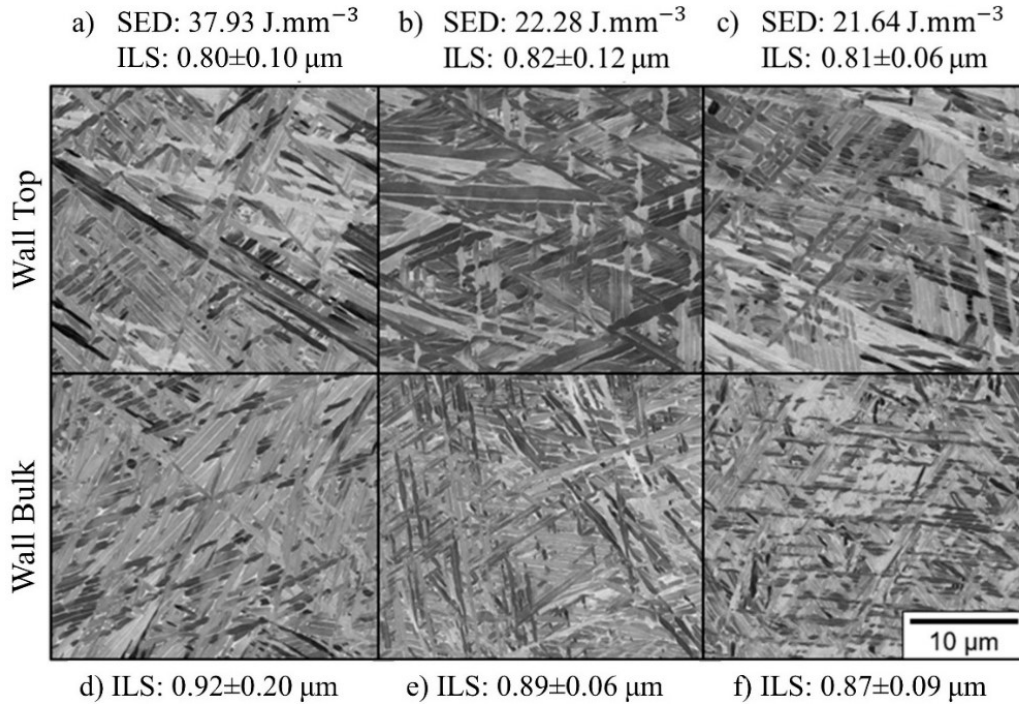


Figure 3-12: Back-scattered electron images of a lamellar microstructure and measured ILS for Specimens 1, 4 and 5 respectively a) – c) wall top, d) – f) wall bulk.

Due to the limited deposition size, it was not possible to extract tensile or fatigue specimens to characterise the mechanical performance with the reduction in SED and refinement of the prior-β grains. However, microhardness measurements of each specimen were conducted to give an indication of the mechanical performance and provide insight into other properties such as yield strength and wear resistance [53]. The average hardness for specimens 1 – 5 was found to be 346.17 Hv ± 11.19; 345.64 Hv ± 9.82; 341.56 Hv ± 13.59; 328.45 Hv ± 17.79 and 325.32 Hv ± 16.31 respectively. The results of the microhardness tests are presented in Figure 3-13. It may be observed that the average hardness of specimens 4 and 5, where prior-β grain refinement had occurred were ‘softer’ than the columnar dominant specimens. Similarly, a larger variance in specimens 4 and 5 was measured, with a minimum hardness measuring ~ 300 Hv reoccurring.

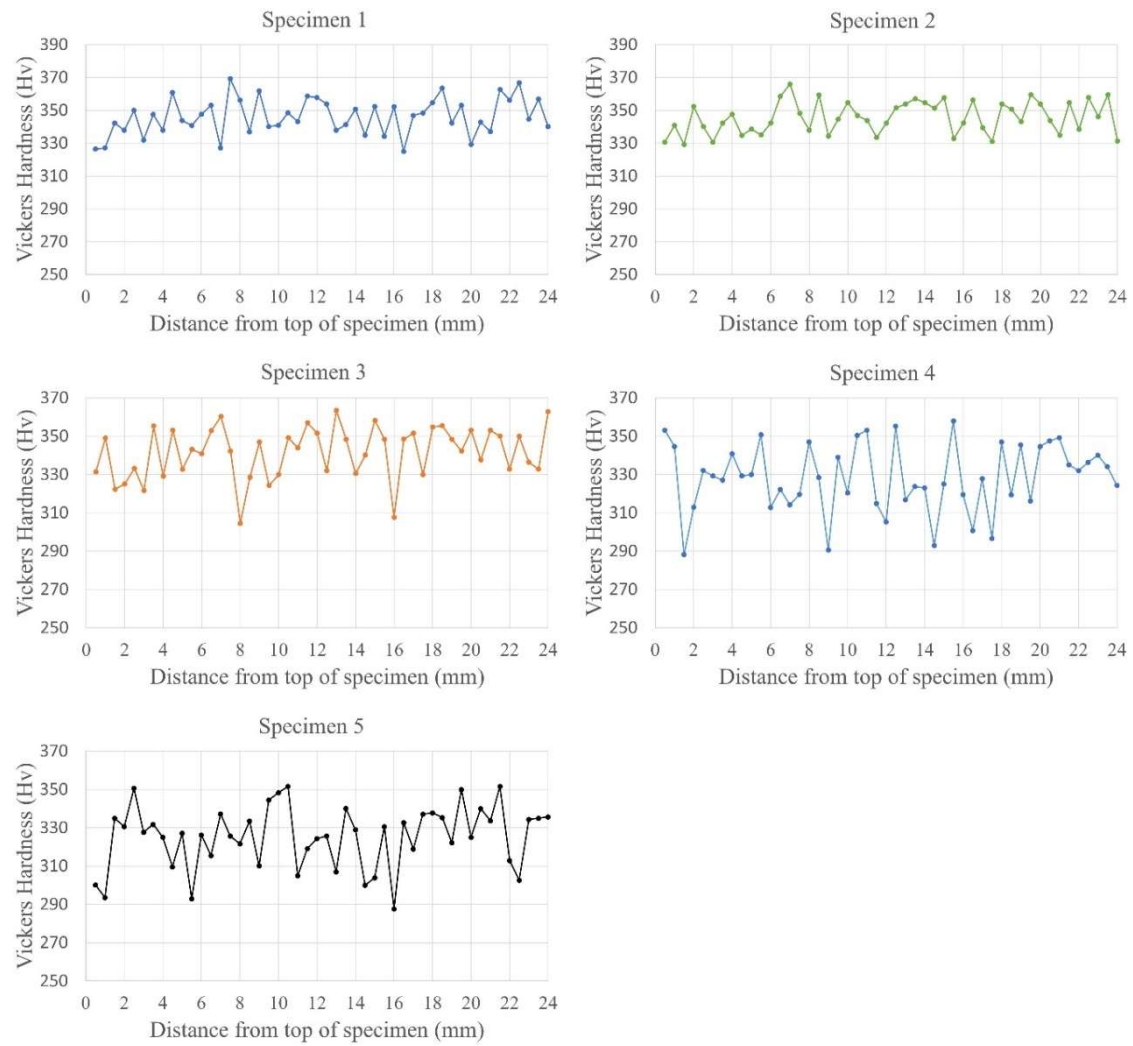


Figure 3-13: Microhardness ($HV0.3$) measurements of specimens 1 – 5 - (1) $37.93 \text{ J} \cdot \text{mm}^{-3}$ (2) $30.39 \text{ J} \cdot \text{mm}^{-3}$ (3) $28.48 \text{ J} \cdot \text{mm}^{-3}$ (4) $22.28 \text{ J} \cdot \text{mm}^{-3}$ (5) $21.64 \text{ J} \cdot \text{mm}^{-3}$.

Given the similarity in ILS spacing, thus effective slip length, which has been demonstrated to be inversely proportional to hardness and strength [54] between the columnar and refined specimens, it was not expected that the value of hardness would diverge as significantly. Whilst further investigation is required to fully characterise the increase in hardness variation, initial investigation of the microstructures demonstrated varying α lamellar morphologies inside the refined prior- β grain specimens as opposed to a consistent Widmanstätten morphology seen across the columnar specimens. The significant difference in layer height as the SED reduced undoubtedly leads to more complex thermal histories and cooling rates in the refined specimens as compared to the columnar specimens. The majority of the previous layer is beta annealed during the successive layer-upon-layer deposition, observed through the closer spacing of the

coarsened α banding. Observed in Figure 3-14 is the microhardness indentations made at an equal spacing below the top of the wall for the columnar prior- β grain specimen 1 and refined prior- β grain specimen 5. It is possible to observe a consistent Widmanstätten α microstructure versus various α morphologies in specimen 5, showing signs of Widmanstätten; acicular; fragmented lamellar; colony and elongated α . These changes in α morphology are most likely responsible for the variation in microhardness as it directly influences mechanical properties as seen in other studies [53–57]. Therefore, whilst the size of prior- β grains has reduced with SED, this introduced variability in the α microstructure morphology. To improve the homogeneity of the α microstructure it is possible to perform a β -anneal heat treatment [12,58], which allows the α microstructure to fully dissolve and using a controlled cooling rate, a uniform microstructure can be generated [59].

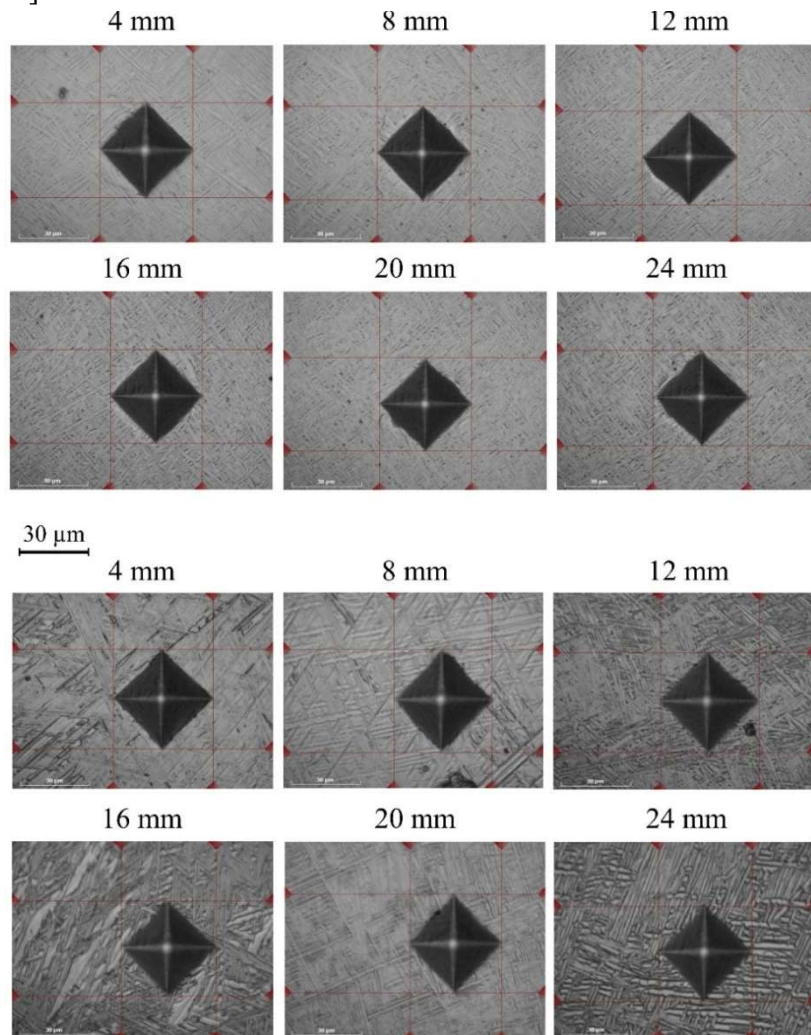


Figure 3-14: Vickers hardness indentations showing localised microstructure of specimen 1 (columnar prior- β grains) (Top) and specimen 5 (refined prior- β grains) (Bottom) at 4 mm spacing below the top of the deposit.

The reduction in the SED as a consequence of the increase in WFS, whilst beneficial to the prior- β grain structure, does present challenges during deposition, such as the change in TM, as discussed. To reduce the SED to the required value poses risk to deposition stability, as the limit of WFS can easily be reached without the introduction of multiple wire feeding. The consequence of maintaining the TS for variable WFS is the influence on the WFS/TS ratio, which effects bead geometry and thus forming quality. As the WFS/TS ratio is increased so too is the material deposited per unit length, leading to an increased layer height and lower forming quality, as the bead width is almost constant for a fixed TS, and consequently a larger surface roughness is generated [60]. In this experiment the effective wall width (EWW) was reduced by 20% from specimen 1 to 5 as surface roughness increased with the reduction in SED. The maximum wall width was reduced by the change in transfer mode from TM2 to TM3 due to the reduction in arc energy transferred to the substrate from arc shading [49]. As may be observed in Figure 3-15, for specimens 1 and 2 the wall width was stable at 7.2 mm while TM2 is active and reduces to a minimum of ~ 6.76 mm when TM3 is activated in specimens 3 – 5. The reduction in forming quality with SED in favour of a refined prior- β grain structure has the potential to reduce the productivity of the manufacturing process as a sufficient bead overlap would be required to achieve homogenous deposits without lack of fusion defects.

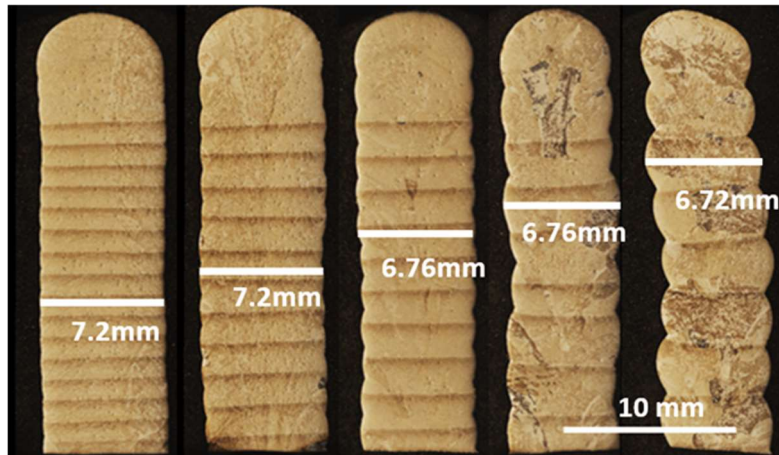


Figure 3-15: Change in wall width and surface roughness as SED is reduced from 37.93 $\text{J} \cdot \text{mm}^{-3}$ (left), 30.39 $\text{J} \cdot \text{mm}^{-3}$, 28.48 $\text{J} \cdot \text{mm}^{-3}$, 22.28 $\text{J} \cdot \text{mm}^{-3}$, 21.64 $\text{J} \cdot \text{mm}^{-3}$ (right).

3.5 Conclusions

The outcome of this study has shown that the as-deposited prior- β grain structure can be controlled during manufacturing without a reliance on post-processing or melt pool agitation. For a fixed heat input, by controlling the specific energy density (SED) of

deposited material, the thermal gradient can be reduced to allow for epitaxial growth to be blocked and competitive dendritic growth to be achieved, with negligible effect on the inter-lamellar spacing (ILS), producing refined prior- β grains. However, whilst the ILS remains consistent, the morphology of the α microstructure changes from a Widmanstätten dominant microstructure to including larger colony and fragmented α lamellar as SED is reduced. This influences the mechanical properties with a reduction in average Vickers hardness and larger variation in the refined prior- β grain specimens over their height as compared to the typical columnar prior- β grain specimens deposited using wire-direct energy deposition. An optimum SED exists before grains revert to a more dominant and previously unseen horizontally tilted grain growth. The change in SED does not appear to have considerable influence over the average peak melt pool temperature as compared to the feedstock transfer mode (TM) used during deposition which generates arc shading at high wire feed speed (WFS) rates. The reduction in SED leads to an unfavourable deposition geometry, however, highlighting that prior- β grain structure control is possible in the as-deposited condition without requiring post-processing.

The outcomes of this study can be summarised as follows:

- 1) For a fixed heat input, a reduction in the SED of deposited material can be used to refine the as-deposited prior- β grain structure and achieve close to an equiaxed morphology with minimal crystallographic texture.
- 2) When the SED of deposited material was reduced beyond an optimum, the morphology reverts to an uncompetitive horizontally tilted grain structure following the maximum thermal gradient from the solidification front at the rear of the melt pool.
- 3) The reduction in SED does not have a large effect on the peak melt pool temperature, which was instead determined by the TM of feedstock during deposition as a result of arc shading.
- 4) The reduction in SED provides greater ILS homogeneity between the top and bulk of the specimen due to a reduction in the α microstructural coarsening within a fixed volume as a result of increased layer height.
- 5) The reduction in SED has negligible effect on the ILS, however, changes the morphology of the α microstructure from Widmanstätten dominant to including

larger colony and fragmented α lamellar creating larger variation in the measured Vickers microhardness.

- 6) A reduction in the SED generates unfavourable surface roughness and reduction in effective wall width due to a decrease in the WFS/TS ratio, culminating in taller deposits with greater curvature.

In conclusion, the impact of this study is significant in laying the foundations for stable deposition of a localised prior- β grain structure in the as-deposited condition through simple modification of the solidification conditions via process control. This level of refinement has not previously been achieved in wire-direct energy deposition of Ti-6Al-4V without reliance on unstable deposition conditions; cold/hot-working; alloy modification or heat treatment. Further work is required to validate the SED hypothesis, in relation to differing process parameters and microstructural nuances that appear to occur in relation to the melt pool shape. However, this method of grain refinement proves promising in order to refine prior- β grains in the as-deposited condition through simple process control alone.

3.5.1 Acknowledgements

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4. The Effect of Melt Pool Geometry on the As-deposited Grain Structure of Titanium Alloys during Wire + Arc Additive Manufacturing

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Abstract

This study demonstrates the effect of specific energy density of deposited material for varying process parameters on the prior- β and β grain structure of Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr during Wire + Arc Additive Manufacturing. A stable droplet transfer mode is maintained to ensure process stability and preventing refinement through melt pool agitation. It was determined that whilst the prior- β grain structure was refined as specific energy density was reduced, the refinement was not primarily caused by a reduction in thermal gradient and increase in nucleation ahead of the solidification front. It was demonstrated that the refinement of the prior- β grains in Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo was directly related to the melt pool curvature, measured via the length/depth ratio. Refinement of the β grains in Ti-5Al-5Mo-5V-3Cr obtained a mixed structure as the length/depth ratio was considerably higher as a consequence of an increased melt pool length hence length/depth ratio. The relationship between length/depth ratio led to an investigation of the grain boundary misorientations via electron back-scattered diffraction, which demonstrated a high volume of 51° $\langle 110 \rangle_\beta$ and 60° $\langle 110 \rangle_\beta$ misorientations corresponding to known easily activated twinning systems in titanium, $\{332\}_\beta$ $\langle 113 \rangle_\beta$ and $\{112\}_\beta$ $\langle 111 \rangle_\beta$ respectively. Hence, dendrite twinning was proposed as a new mechanism for prior- β and β grain refinement during deposition of titanium alloys.

4.1 Introduction

Wire + Arc Additive Manufacturing (WAAM) is a direct energy deposition process that is used to create near-net shape metallic components utilising an arc power source and wire feedstock to deposit successive layer-by-layer weld beads [1]. WAAM is ideally suited to the creation of medium to large scale components given its somewhat low resolution [2], as well as its intrinsic capability to increase productivity and accelerate time to market compared to traditional subtractive machining or forging techniques [3]. Both simple and medium complexity geometries can be generated by WAAM through control of a multitude of processing parameters. Typically, the microstructural characteristics and subsequent mechanical properties can be tailored in the as-deposited condition [4], or via post-processing such as rolling and peening [5,6]. WAAM is able to exploit numerous metallic alloy systems and has shown efficacy in aluminium, titanium and steel deposition [7–10], as well as refractory metals including tungsten and molybdenum [11]. A basic WAAM system can be integrated into an existing manufacturing suite with relatively ease, consisting of a computer numerical control (CNC) or robotic manipulator, arc power source, automated wire feeding system and shielding from oxygen (global or local). Therefore, WAAM boasts a low capital investment cost, relative to subtractive manufacturing or forging [1,7] coupled to reduced manufacturing costs, and has the potential to revolutionise the manufacturing industry [12].

Ti-6Al-4V forms a major focus of additive manufacturing research as it is a widely used commercial alloy known for its high specific strength and corrosion resistance. Similarly, as a costly and difficult material to extract, process and manufacture [9], it is ideally suited for WAAM with associated low manufacturing cost [1]. A common measure within the aerospace industry is the buy-to-fly (BTF) ratio, which measures the material required to create a component versus the amount of material remaining on the final finished component. Whilst there is a trade-off between deposition speed and surface finish, WAAM can reduce the typical BTF from 10 – 20 to < 1.5 and reduce the manufacturing lead time from months to mere hours [1]. However, general limitations of the WAAM process exist. A continuous thermal cycling occurs during deposition leading to complex thermal histories and accumulation of residual stresses that can alter physical shape, i.e. distortion, and affect grain structure and consequently component mechanical properties

[13,14]. A clear example of this is the layer bands that may be observed in etched Ti-6Al-4V samples, highlighting the α microstructure that is subjected to coarsening as a direct result of a β -anneal heat treatment that occurs for every layer of deposition [14]. Additionally, during deposition it is imperative that sufficient shielding from oxygen be maintained. Titanium exhibits a high reactivity with oxygen, which is an α -phase stabiliser and severely embrittles the material in a process known as α -case hardening, which has severe implications on the ductility of the material [15].

The primary limitation of the deposition of titanium alloys, particularly Ti-6Al-4V using WAAM, are the innate metallurgical challenges that persist in regard to solidification. In the as-deposited condition, titanium alloys exhibit highly textured $\langle 100 \rangle_\beta$ coarse columnar prior- β grains in relation to the build direction (BD) [16]. Visible to the naked eye, these grains extend from the bottom of a deposit to the top, reaching up to centimetres in width [16]. The result is an anisotropic mechanical behaviour observed primarily through the ductility between the horizontal and vertical directions, due to the inequitable distribution of grain boundary α across an equivalent volume [16,17]. To prevent anisotropic behaviour in Ti-6Al-4V, therefore, requires the refinement of the β grains that form in the initial stages of solidification, changing their morphology from a columnar to an equiaxed structure. In the as-deposited condition this has proven difficult due to the alloy constitution of Ti-6Al-4V and high thermal gradients associated with the WAAM process [18,19]. During deposition, a low level of constitutional supercooling exists due to a lack of solute partitioning from the primary alloying elements of aluminium and vanadium [19]. Reported partition coefficients for aluminium range from 1.01 – 1.13 [20], whilst in vanadium, 0.89 – 0.96 [21] have been reported. Therefore, there is little deviation of the enriched solute temperature at the solidification front as compared to the bulk material. This ensures there is little chance for random competitive growth via homogenous nucleation within the melt pool and instead growth occurs via an epitaxial growth mechanism that requires substantially less free energy [22], which remains competitive for grains in line with the maximum thermal gradient [23]. This mechanism occurs when solidifying atoms attach themselves to the pre-existing partially melted grain lattice of the previously deposited layer [19]. Consequently, in the as-deposited condition, prior- β refinement mechanisms of titanium alloy systems have focused on melt pool agitation, thermal intervention or inoculation of growth restricting elements such as boron

and yttrium to induce refinement [24–31]. Post-processing techniques such as rolling and peening which introduce plastic strain and promote the recrystallisation of β grains during subsequent remelting have also demonstrated success in prior- β refinement [5,6,32,33]. All these aforementioned methods exhibit additional capital investment cost and have the potential to limit design freedom [33] or lead to the production of ‘dirty’ alloys, scattered with unwanted intermetallic compounds detrimental to mechanical properties [29,34].

From a purely as-deposited processing perspective, to enable the refinement of Ti-6Al-4V in the as-deposited condition has yielded limited success. Wang et al. [35] unintentionally demonstrated that through increasing the deposition rate for a fixed arc energy, the introduction of a negative thermal gradient at the top of the melt pool surface to block epitaxial growth could be achieved, however, this was reliant on the penetration of the melt pool surface with the feedstock material. A further study by Wang et al. [25], confirmed an identical effect through the deliberate penetration of the melt pool with the feedstock material. It was postulated that the introduction of the feedstock material to penetrate the melt pool surface encouraged heterogeneous nucleation to occur at the surface of the submerged wire before it was able to melt. The nucleated dendrites could then breakaway into the melt pool and block epitaxial growth [25,35]. Additionally, the penetration of an un-melted wire would provide agitation of the melt pool, triggering nucleation ahead of the solidification front and stimulating dendrite fragmentation where epitaxially generated dendrites introduced at the solidification front breakaway and are carried through the melt via fluid dynamics and continue to grow, blocking epitaxial growth [24,35]. However, as it is conditional on an unstable deposition condition, reliance on this method should be avoided as discussed by Rios et al. [36]. Similarly, this feedstock transfer mode can easily lead to lack of fusion defects; unstable deposition geometry due to hitting the bottom of the melt pool and skating to one side; plus the inherent risk of equipment damage.

It has been demonstrated by Zhang et al. [37] that through continuous alteration of the processing parameters layer-upon-layer, the refinement of Ti-6Al-4V can be achieved during powder-direct energy deposition. The method is reliant on alternating the laser power or deposition speed to alter the penetration depth of the successive deposit, such that it does not erase equiaxed grains formed at the top of the previous layer. This allows a small amount of epitaxial growth from the refined grains, rather than continuous

epitaxial growth throughout the specimen of the $\langle 100 \rangle_\beta$ preferentially orientated grains. However, such an approach is not without limitation, as the continual change in power and travel speed leads to a continual change in α interlamellar spacing as the heat input and cooling rate is consistently fluctuating. However, during the study only the average values were reported and no indication of variation given [37]. A foreseeable limitation of this method is likely to be in the noticeable differences in bead geometry due to reduction of travel speed required to achieve refinement when building complex geometries, raising concerns around scalability and applicability. Whilst successful for a powder-direct energy deposition process, this method may not be applicable to WAAM due to large differences in melt pool geometry, heat inputs and cooling rates [7,24]. Bermingham et al. [27] attempted a similar approach for the deposition of Ti-6Al-4V during WAAM, by increasing the solidification rate to encourage prior- β grain refinement, but were unsuccessful due to a change in the melt pool geometry negatively affecting the thermal gradient. The increase in travel speed led to a reduction in the wire feed speed/travel speed (WFS/TS) ratio, which is known to reduce the layer height [38]. The combined impact was an overall increase in the thermal gradient, observed experimentally through the use of pyrometry, resulting in prior- β grain refinement being harder to achieve. However, the impact of melt pool geometry cannot be ignored in regard to prior- β grain refinement of Ti-6Al-4V.

Wang et al. [39] considered the effect of deposition strategy to alter the microstructural characteristics in the as-deposited condition. By maintaining a consistent set of deposition parameters, except for the interlayer dwell time, some success in refining the prior- β columnar morphology to an equiaxed structure was demonstrated. However, variation and mixed structures were observed within a single process variable set, indicating that this method of refinement is inherently uncontrollable. The refinement observed was determined to be a recrystallisation of the prior- β grains as a consequence of the increase in stored energy by α martensite (observed as large dislocation densities). This is not something typically seen in WAAM, as cooling rates that drive martensitic α are rarely achieved and typically avoided [40]. For this reason, heat treatments of prior- β grains rarely leads to recrystallisation, as during reheating, the nucleation and growth of the β phase is after an initial recovery of the $\alpha + \beta \rightarrow \beta$ [41]. This transition occurs by movement of the α/β interface until only β exists. It is believed that the nucleation of new β

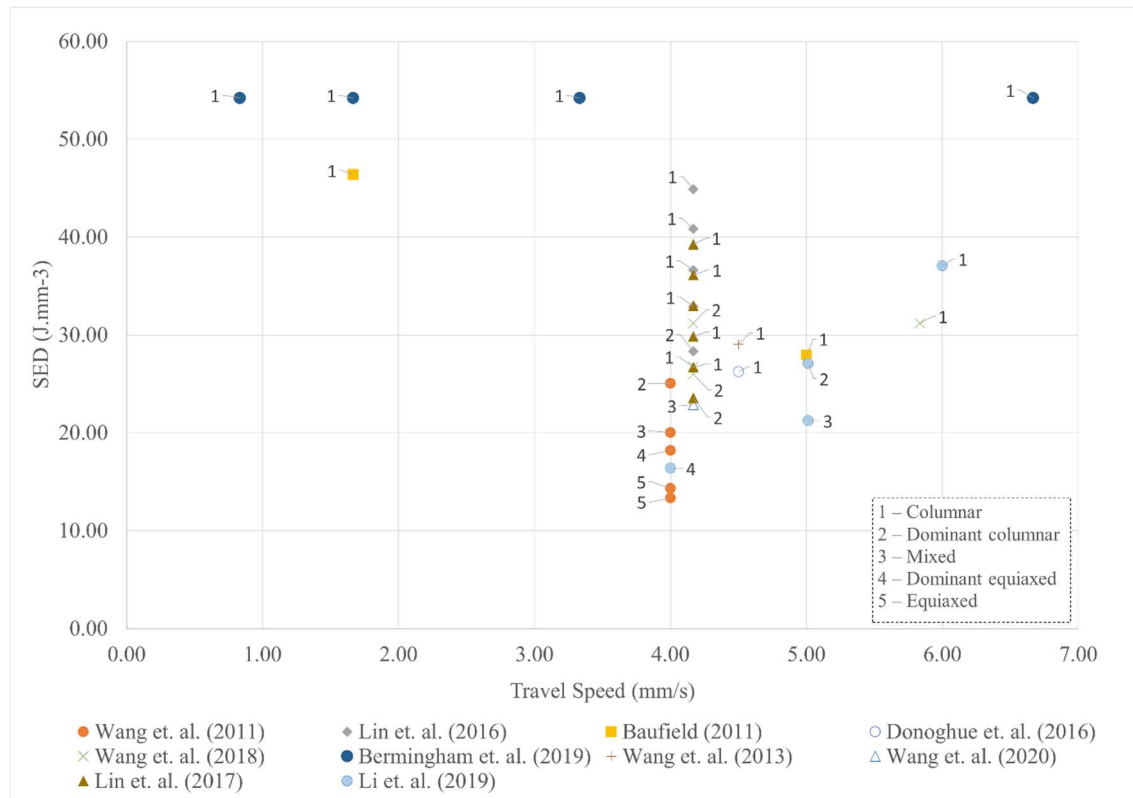
orientations cannot occur as the shear stress is too low to induce recrystallisation [41,42]. The phenomenon reported by Wang et al. [39] relied upon the stored energy surrounding the α martensite that seeds recrystallisation and is similar to the mechanism expressed in rolling or peening [5,32]. Others have corroborated these results through rapid heat treatments [41], rather than influencing the cooling rate during deposition. The challenge of employing this grain refinement mechanism on the large-scale deposition of WAAM components is the general avoidance of the cooling rates required which would lead to residual stress. Residual stress is identified as one of the major defects of components produced with WAAM and leads to major distortion and cracking [43], and methods such as rolling [44] and path planning strategies are implemented to avoid such residual stresses [45].

It would prove a definitive step for the deposition of titanium components with WAAM if both controlled geometrical and microstructural characteristics could be achieved without the requirement for post-processing, compositional alteration or unstable and undesirable processing conditions. Recently a study by Wainwright et al. [4] demonstrated that the refinement of the prior- β grain structure and subsequent removal of texture can be achieved through a reduction in the specific energy density of deposited material (SED), whilst maintaining a stable processing condition i.e. a reduction in the energy per unit volume of material being deposited. Using pyrometry to measure the peak melt pool temperature, Wainwright et al. [4] were able to calculate that a reduction in the SED led to a decrease in the thermal gradient, using a linear thermal gradient approximation developed by Bermingham et al. [27]. This reduction in thermal gradient appeared to increase the opportunity for nucleation ahead of the solidification front and allowed for random competitive dendritic growth, blocking columnar epitaxial prior- β grain growth. The methodology relied on an increase in the wire feed speed (WFS) whilst maintaining a consistent arc energy and travel speed (TS), altering the WFS/TS ratio. As previously described, the increase in WFS/TS has been determined to influence the bead geometry [38]. Consequently, a reduction in effective wall width by 20% was observed as the SED reduced to meet the conditions required to achieve refined prior- β grain growth as compared to columnar [4]. Interestingly, the results demonstrated an optimal value of SED existed before prior- β grains reverted to a horizontally dominant elongated morphology. The grains tilted towards the direction of the heat source travel direction,

indicating that prior- β grain morphology was also linked to the melt pool shape, as grains tilted to follow the maximum thermal gradient perpendicular to the solidification front [34]. A change in melt pool shape and grain morphology has also been demonstrated by Li et al. [46] for Ti-6Al-4V deposition, where the increase of current in a resistive heating circuit linked to the wire allowed a lower arc current to be used for deposition. This had a severe impact on the melt pool geometry, which became taller and narrower. It was suggested that the lower arc energy was responsible for the prior- β grain refinement observed. However, this method was reliant on penetration of the melt pool, to complete the resistive heating circuit, which can lead to dendrite fragmentation and heterogeneous nucleation at the wire. Unfortunately, it was not possible to identify the mechanism of refined prior- β grain growth explicitly and may only be coincidental that the arc energy reduction was affecting the prior- β grain morphology. The change in maximum thermal gradient perpendicular to the solidification front cannot also be discounted due to the significant change in melt pool shape.

The proposed SED parameter by Wainwright et al. [4] takes into account the volume of deposited material, something that is not considered when using heat input, which only considers the arc energy and travel speed of deposition. If the SED is plotted against the travel speed used during deposition this can be used to correlate all processing parameters against prior- β grain morphology. Normally the grain structure prediction has been solely dependent upon the calculation of thermal gradient (G) and solidification rate (R) post deposition [27], which is difficult to measure. Experimentally, to measure thermal gradient requires acquisition of melt pool temperature data, which can be obtained by 'harpooning' thermocouples into the melt pool [14]. However, this approach provides no guaranteed placement or survival, and there remains a lag time between insertion and data collection. Hence, whilst this method captures important aspects of the cooling rate, it does not provide reliable data for the temperature during solidification. Solidification rate is more easily dealt with and is generally equated to the travel speed during deposition [27] although this neglects the dependence on the angle of curvature perpendicular to the solidification front relative to the deposition direction [34], which cannot be directly measured during deposition. In Ti-6Al-4V, curvature cannot be observed post deposition and etching due to deposition of a single alloy and no distinguishable solidification front.

The SED can be calculated prior to deposition and appears to predict grain morphology [4]. Figure 4-1 considers previous studies that have attempted to refine the prior- β grain structure of Ti-6Al-4V during WAAM (providing sufficient processing parameters reported for calculation) in as-deposited condition utilising a stable processing condition. It may be observed that when the SED is reduced, or TS increased, a level of grain refinement is obtained, moving through a columnar dominant to equiaxed dominant structure, indicating agreement with the results reported by Wainwright et al. [4]. This may be attributed to the drop in thermal gradient as SED is reduced and compression of solute at the dendrite tip as TS is increased, maximising the total constitutional supercooling [18,47] and hence opportunity for nucleation ahead of the solidification front.



increasing the total arc energy through increased current. Further validation of the refinement mechanism for the increased opportunity for nucleation ahead of the solidification front was investigated through the deposition of Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr. These alloys contain increasing levels of growth restriction elements, particularly molybdenum that has slow diffusivity in titanium [19], which helps to prevent solid state grain growth during reheating, limiting the size of solidified grains and providing a greater growth restriction factor. Therefore, a greater level of constitutional supercooling was expected, to enable the columnar-to-equiaxed transition (CET) to occur at respectively higher SED levels to the original study by Wainwright et al. [4] (hereby referred to as the ‘base study’).

4.2 Methodology

During this study a total of twenty samples were deposited in four subsets of five specimens, each related to a specific processing condition (decreased travel speed and increased arc current) and material deposited (Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr) in relation to the base study [4]. An identical experimental methodology was adopted to that of the base study [4]. All samples were deposited on to Ti-6Al-4V substrates (175 mm x 50 mm x 10 mm) clamped in each corner to an aluminium backing plate. Deposition was conducted using a TECARC PLASWELD 400 DC power source and PWP Viper plasma torch. 150 mm long successive single pass single direction linear tracks were deposited, controlled via a Aerotech CNC 3 axis gantry system. A dual wire feeding system comprised of two Migatronik KT4 wire feeders was utilised to front-feed 1.2 mm diameter wire to the centre of the arc with a 10° offset. Deposition occurred within a globally shielding environment purged with UN1006 Pureshield Argon and held to < 100 PPM oxygen continuously measured by a Argweld PurgEye 600. The experimental setup and schematic may be observed in Figure 4-2. The composition of wire feedstock is provided in Table 4-1 by the manufacturer (Perryman) subject to their quality assurance techniques at the point of manufacture. The processing parameters for each subset are listed in Tables 4-2a)-d).

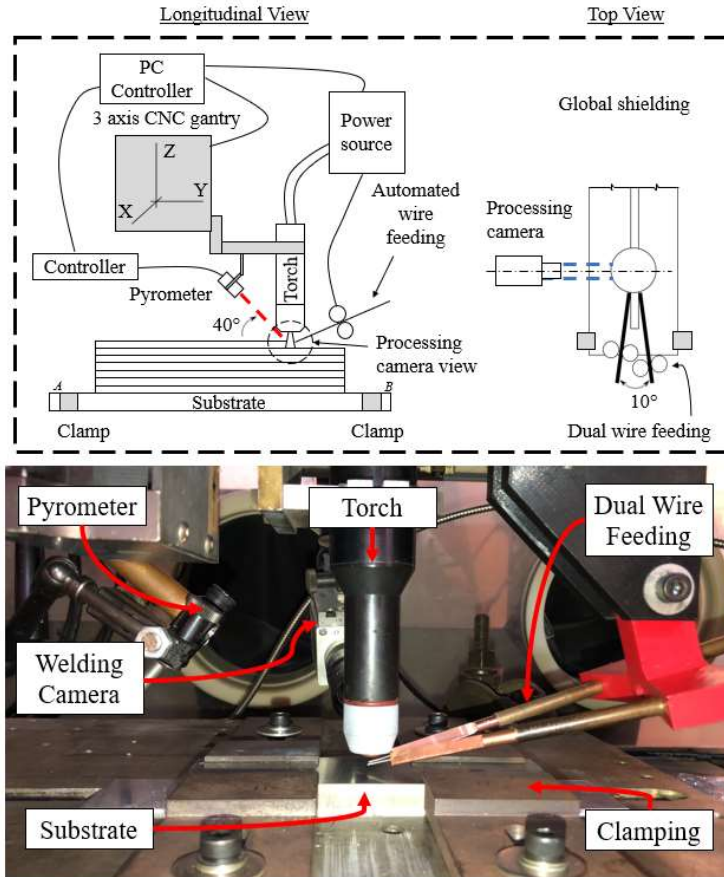


Figure 4-2: Experimental setup used for all deposition (T) Schematic (B) In-situ.

Table 4-1: Composition of feedstock material (wt %)

Material	Element (wt %)										
	O	N	Sn	Fe	Al	V	Si	Mo	Cr	Zr	Ti
Ti-64	0.15	0.008	-	0.18	6.14	3.94	0.012	-	-	-	BAL
Ti-6242	0.12	0.003	2.00	0.03	6.00		0.09	2.00	-	3.90	BAL
Ti-5553	0.129	0.002	0.01	0.43	5.00	4.92	0.02	4.86	2.89	0.09	BAL

Table 4-2a: Processing parameters subset 1: Ti-6Al-4V decreased travel speed

ID #	Voltage (V)	Current (A)	Travel Speed (mm.s ⁻¹)	Wire feed speed (mm.s ⁻¹)	SED (J.mm ⁻³)
1.1	18.10	106.30	3.00	26.00	39.25
1.2	17.98	106.10	3.00	34.11	29.67
1.3	17.79	105.90	3.00	36.82	27.15
1.4	18.35	105.70	3.00	46.33	22.22
1.5	17.78	106.70	3.00	50.40	19.96

Table 4-2b: Processing parameters subset 2: Ti-6Al-4V increased current

ID #	Voltage (V)	Current (A)	Travel Speed (mm.s ⁻¹)	Wire feed speed (mm.s ⁻¹)	SED (J.mm ⁻³)
2.1	20.50	160.30	4.00	46.00	37.83
2.2	20.52	160.10	4.00	57.44	30.29
2.3	21.45	157.50	4.00	63.00	28.30
2.4	21.40	157.40	4.00	80.00	22.28
2.5	20.53	160.10	4.00	85.00	20.47

Table 4-2c: Processing parameters subset 3: Ti-6Al-2Sn-4Zr-2Mo

ID #	Voltage (V)	Current (A)	Travel Speed (mm.s ⁻¹)	Wire feed speed (mm.s ⁻¹)	SED (J.mm ⁻³)
3.1	17.30	108.20	4.00	27.38	36.27
3.2	19.51	106.40	4.00	35.87	30.68
3.3	17.95	107.00	4.00	40.12	25.33
3.4	18.55	107.40	4.00	47.20	22.33
3.5	18.13	108.20	4.00	52.86	19.65

Table 4-2d: Processing parameters subset 4: Ti-5Al-5Mo-5V-3Cr

ID #	Voltage (V)	Current (A)	Travel Speed (mm.s ⁻¹)	Wire feed speed (mm.s ⁻¹)	SED (J.mm ⁻³)
4.1	17.91	106.50	4.00	27.84	36.33
4.2	17.35	107.90	4.00	33.60	29.47
4.3	18.10	107.30	4.00	40.52	25.43
4.4	17.62	107.5	4.00	46.16	21.74
4.5	17.99	107.20	4.00	53.21	19.13

When attempting to replicate equivalent processing parameters from the base study some variance in SED existed due to unavoidable equipment limitations. For example, WFS is a dominant factor of the SED calculation. The remote control unit of the Migatron wire feeders uses 1% increments of maximum WFS available, dependent on the feed liner tension this translated to $\sim 1.40 \text{ mm.s}^{-1}$ incremental blocks. The current selected from the power source was 105 A, however, micro-fluctuations in contact tip work distance, surface finish of the substrate and wear of tungsten electrode generate a small process fluctuation. Therefore, the processing parameters of all subsets were selected such that the SED values of the base study by Wainwright et al. [4] were replicated as closely as possible, i.e. 37.93 J.mm^{-3} , 30.39 J.mm^{-3} , 28.48 J.mm^{-3} , 22.28 J.mm^{-3} and 21.64 J.mm^{-3} . In summary, with respect to the base study, subset 1 utilised a reduced travel

speed, subset 2 an increased arc energy, subset 3 changed feedstock composition to Ti-6Al-2Sn-4Zr-2Mo and subset 4 changed feedstock composition to Ti-5Al-5Mo-5V-3Cr.

During the deposition of all subsets, 50 mm tall walls were deposited to provide specimens for microstructural characterisation in the form of 30 mm x 30 mm longitudinal sections, machined to the central plane. Microstructural samples were mounted on conductive phenolic resin via a hot mounting press and mechanically polished with consecutively higher grades of silicon carbide paper from 240 grit to 2000 grit. A final polish was conducted using colloidal silica and oxalic acid before etching with Kroll's reagent for ~ 10 seconds to reveal the microstructure. 20 mm of 'waste' material was first deposited to account for changes in conduction through the substrate, the primary method for heat extraction. This effect can be monitored by the stability of the bead geometry measured in width and height. In addition, for the Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr specimens this provided a buffer for composition stability after mixing and diffusion with the Ti-6Al-4V substrate in the initial layers. The composition of the microstructural specimens was confirmed to have contained no Ti-6Al-4V contaminant via energy-dispersive X-ray spectroscopy (X-EDS).

During deposition all layers were cooled naturally for 60 seconds of ambient cooling before a cooling line containing UN1006 Pureshield Argon was used to apply forced convection to a pre-deposition temperature of < 40°C. This was conducted to ensure that variability in the pre-deposition temperature was removed as the heat extraction rate and thermal mass changed after the deposition of each new layer (a pre-defined cooling time would not account for this and lead to inconsistencies in pre-deposition temperature). The purpose of allowing 60 seconds ambient cooling is to not influence the α microstructure generated during the $\beta \rightarrow \alpha + \beta$ phase transformation, as this allowed sufficient time for the material to cool and be unaffected by forced convection.

Where possible, a Sensortherm Metis M311 2-colour pyrometer was used to monitor the melt pool temperature at a point 2 mm behind the arc centre, at a 120 mm focal length and an angle of 40° to the substrate with a 15 ms response time. This was to allow for calculation of the thermal gradient, using the method proposed by Bermingham et al. [27] in conjunction with the known solidification temperature and measured layer height. This point was selected as the point closest to the arc centre where the melt pool temperature

is hottest, within the spatial limitations of the setup, and gave an ovular spot size of 2.2 mm x 1.6 mm. An emissivity of 0.36 was used as extrapolated from existing literature on high temperature liquid titanium [48]. The average melt pool temperature was used in the calculation taking into account standard error [49] and an instrumentation error of 0.3% as specified by the manufacturer.

During deposition a Xiris XVC-1100 was used to monitor the melt pool and feedstock transfer mode to ensure process stability and consistent ‘droplet’ transfer mode. To ensure high image quality the camera aperture was closed to the manufacturers minimum whilst using a rolling shutter mode and 10 μ s exposure. In all cases a Xiris 50 mm lens was used and protected with a Xiris UV filter and clear glass spatter protection window.

Electron back scatter diffraction (EBSD) analysis was conducted using a Thermo Scientific Apreo C FEG-SEM at 20 kv accelerating voltage and 51 nA beam current at a step size of 15 μ m and processed using Oxford Instruments AztecCrystal software. The allotropic nature of Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo means that it endures a solid-state transformation from $\beta \rightarrow \alpha + \beta$ during cooling, therefore, the β phase cannot be observed directly at room temperature. However, the transformation follows Burger’s orientation relationship (BOR) i.e. $\{110\}_{\beta} // \{0001\}_{\alpha}$ and $\langle 111 \rangle_{\beta} // \langle 0001 \rangle_{\alpha}$ [20], which allows prior- β grain reconstruction based off explicit orientation relationships between α variants and parent grain β . The acquired room temperature $\alpha + \beta$ phase data was subject to parent grain reconstruction developed by Davies and Wynne [50,51], with up to 3° divergence from BOR considered to be part of the same grain and up to a 2° misorientation from a particular variant accepted. Quantitative analysis of the prior- β reconstructions was conducted using Oxford Instruments AztecCrystal software and reported in equivalent circle diameter with all grains < 200 μ m omitted owing to potential reconstruction errors. Due to the volume of specimens present in this study, only specimens deemed of interest were chosen for EBSD due to the large resource requirement, typically those that showed some form of prior- β grain refinement. For optical microscopy a Hirox RH-2000 microscope was utilised with large area mapping at 50x magnification.

Microhardness measurements were conducted using an Innovatest Falcon 503 employing the Vickers method. A 300 g load cell was selected with an indentation of 10 seconds and

0.5 mm indent separation recommended by the manufacturer. A total of 50 measurements were taken along the central line of the specimens, from the top to bottom of the specimen post-polishing and EBSD analysis.

4.3 Results and Discussion

The results of this study are discussed in relation to the those of the base study by Wainwright et al. [4], considering the refinement of WAAM Ti-6Al-4V in the as-deposited condition. For context, the base study EBSD prior- β grain reconstructions with inverse pole figure (IPF) colouring relative to the build direction may be observed in Figure 4-3 (reproduced with the permission of the authors). It may be observed that as the SED was reduced, a breakdown in the highly textured columnar grain structure occurred highlighted in Figures 4-3a)-c), to a refined grain structure in Figure 4-3d), before apparent tilting to the horizontal direction, in line with the direction of deposition in Figure 4-3e). Whilst the horizontal tilting exhibited a preferential growth direction, there was a significant lack of texture as compared to the columnar specimens. In the optimal case (Figure 4-3d)), the average grain size was calculated as $820 \mu\text{m} \pm 22 \mu\text{m}$ with an average fitted ellipse aspect ratio of 1.83 ± 0.03 , as compared to the columnar prior- β structure observed in Figure 4-3a) with an average grain size of $1797 \mu\text{m} \pm 219 \mu\text{m}$ and fitted ellipse aspect ratio of 3.94 ± 0.26 , hence indicating a significant change in both average grain size and shape. The pole figures for the columnar dominant specimen (Figure 4-3a) and refined specimen (Figure 4-3d) are presented in Figure 4-4 (reproduced with permission of the author) from the perspective of the build direction. As may be observed, there is a complete breakdown in texture as the SED was reduced.

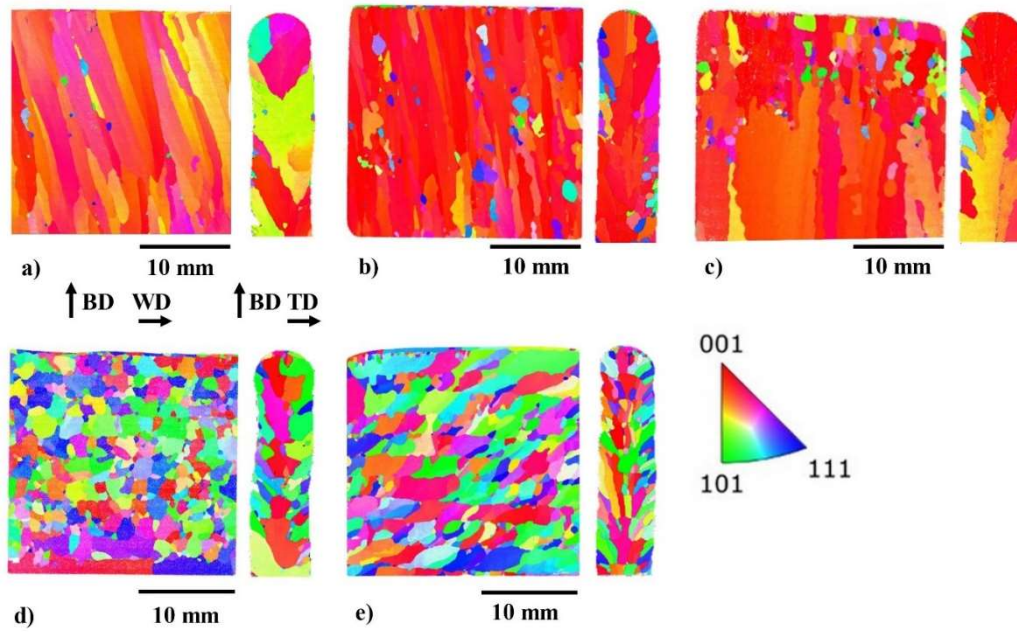


Figure 4-3: IPF prior- β reconstructions from the base study by Wainwright et al. [4] depositing Ti-6Al-4V a) $37.93 \text{ J} \cdot \text{mm}^{-3}$ b) $30.39 \text{ J} \cdot \text{mm}^{-3}$ c) $28.48 \text{ J} \cdot \text{mm}^{-3}$ d) $22.28 \text{ J} \cdot \text{mm}^{-3}$ e) $21.64 \text{ J} \cdot \text{mm}^{-3}$.

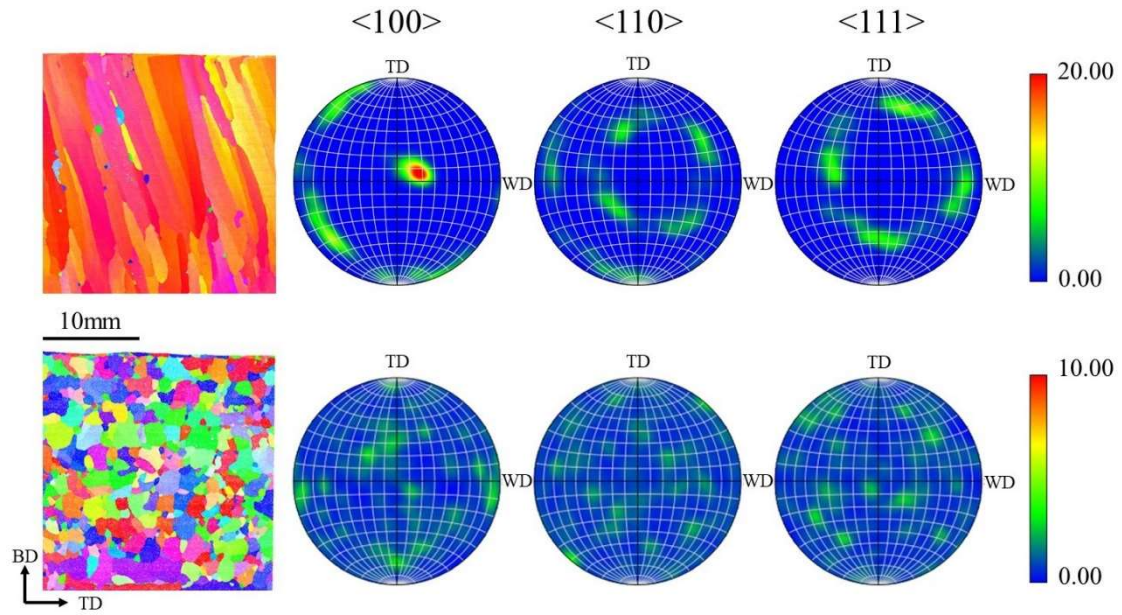


Figure 4-4: Pole figures demonstrating reduction in texture from the columnar ($37.93 \text{ J} \cdot \text{mm}^{-3}$) to equiaxed ($22.28 \text{ J} \cdot \text{mm}^{-3}$) Ti-6Al-4V specimens from the base study [4], alongside prior- β IPF reconstructions with respect to build direction (BD). Note the decrease in intensity scale between the top and bottom scales and lack of intensity in the equiaxed specimen.

4.3.1 Reduced Travel Speed

The macrographs of the Ti-6Al-4V subset 1 specimens may be observed in Figure 4-5. With respect to the base study [4], the deposition conditions are equivalent with only a reduction in TS of deposition implemented, with the intention to make refinement more difficult to achieve by reducing the solidification rate [52]. It was anticipated a lower SED would be required to achieve refinement. Qualitative analysis of the optical macrographs reveals that as the SED was reduced, there was a breakdown in prior- β grain structure. Columnar grains may be observed at 39.25 J.mm^{-3} and 29.67 J.mm^{-3} before exhibiting evidence of refinement at 27.15 J.mm^{-3} , where a combination of horizontally tilted and equiaxed grains are manifested. An optimal level of grain refinement may be observed at 22.22 J.mm^{-3} , with apparent equiaxed grains distributed throughout the specimen. Finally, at 19.96 J.mm^{-3} the prior- β grain structure was dominated by horizontally orientated rows of single grains sandwiched between rows of finer equiaxed grains.

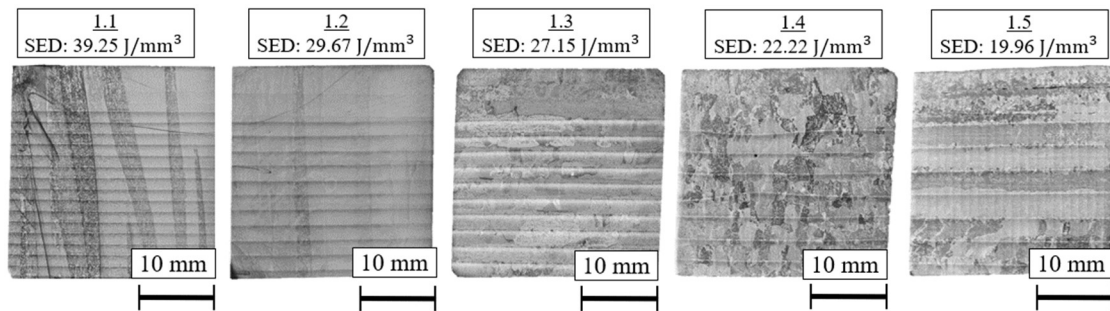
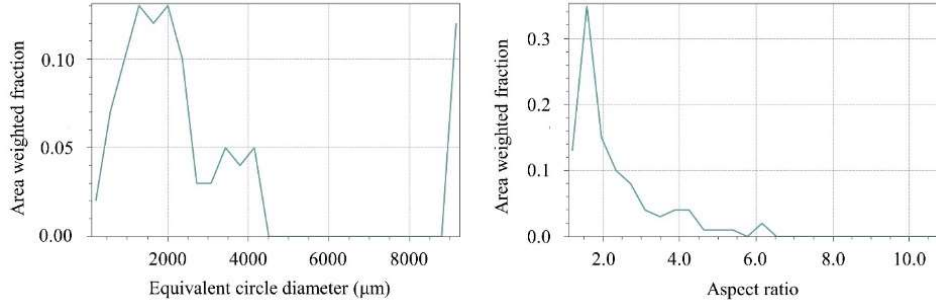


Figure 4-5: Light macrographs of etched longitudinal specimens of Ti-6Al-4V subset 1 demonstrating a breakdown in columnar grain structure as SED is reduced from 39.25 J.mm^{-3} to 22.22 J.mm^{-3} before horizontal grain growth observed across the width of specimen 1.5 at 19.96 J.mm^{-3} .

Specimens 1.4 and 1.5 were selected for EBSD analysis where there was the largest evidence of prior- β grain refinement and an interesting horizontal grain structure. EBSD prior- β grain reconstruction of specimens 1.4 and 1.5, enabled the grain size (in terms of equivalent circle diameter) and aspect ratio to be measured to indicate the level of refinement. In the optimally refined specimen 1.4, the number of grains identified equates to 501 individual grains, a mean equivalent circle diameter of $840 \mu\text{m} \pm 34 \mu\text{m}$ and aspect ratio of 2.29 ± 0.05 . In specimen 1.5, the number of grains identified was 1152 with a mean equivalent circle diameter of $599 \mu\text{m} \pm 18 \mu\text{m}$ and aspect ratio of 2.02 ± 0.03 , however, specimen 1.5 is overwhelmingly dominated by the sheer volume of fine grains sandwiched between the horizontal ones. Figure 4-6 presents the grain size distributions

for specimens 1.4 and 1.5. Given the number of grains present in both specimens being relatively small it is recommended that these results are indicative of grain size.

Specimen 1.4



Specimen 1.5

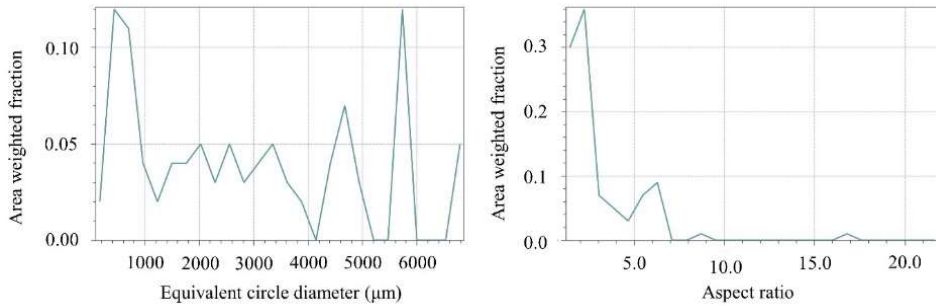


Figure 4-6: Grain size and aspect ratio distribution by area weighted fraction for Ti-6Al-4V specimens 1.4 ($22.22 \text{ J} \cdot \text{mm}^{-3}$) and 1.5 ($19.96 \text{ J} \cdot \text{mm}^{-3}$).

In specimen 1.4 it is clear to see that grains $< 2000 \mu\text{m}$ dominated the majority of the sample with a particularly equitable distribution between $1000 - 2000 \mu\text{m}$. This was not dissimilar to the base study [4], which indicated a comparable distribution of grain size and an almost identical mean equivalent circle diameter of $821 \mu\text{m} \pm 23 \mu\text{m}$. The level of prior- β grain refinement was also confirmed by the low aspect ratio, dominated by < 2 grains. In specimen 1.5, it is clear to observe a large number of fine grains ($200 - 1000 \mu\text{m}$) dominated a large portion of the total specimen area. Whilst this accounts for some of the equiaxed prior- β grains observed near the top of the specimen, this can be mostly attributed to the fine $\langle 100 \rangle_{\beta}$ preferentially orientated grains. In specimen 1.5 a larger variation in equivalent circle diameter was observed compared to specimen 1.4 as a consequence of the differing prior- β grain morphologies. The horizontally orientated grains demonstrated the largest equivalent circle diameter, medium size refined prior- β grains were observed in the final layers and fine equiaxed prior- β grains sandwiched between the horizontally orientated gains. The aspect ratio distribution showed that grains < 2.0 dominated, again largely determined by the number of fine equiaxed prior- β grains

that exist. Note the small peak at ~ 6 for the presence of the horizontal grains that also hold a significant portion of the specimen total area.

The prior- β grain reconstructions with IPF colouring in respect to the build direction and standard titanium cubic pole figures may be observed in Figures 4-7 and 4-8 for specimens 1.4 and 1.5 respectively. It is clear in Figure 4-7 that a refinement of the prior- β grains had occurred with a reduction in the SED. With regards to the grain size and aspect ratio they were similar in morphology to the equivalent SED specimen of the base study. Conversely, a more strongly retained $\langle 100 \rangle_{\beta}$ // BD texture was present across large areas of the specimen. In comparison to the base study this indicated that preferential grain growth had occurred and continued to dominate the nature of solidification and outcompete non-textured grains that may form by nucleation in the melt pool ahead of the solidification front. In the prior- β grain reconstruction of specimen 1.5 (Figure 4-8), large horizontally orientated non-textured grains appeared, sandwiched between layers of fine, equiaxed morphology textured grains. As indicated by the pole figures, a $\langle 100 \rangle_{\beta}$ // BD texture was only somewhat retained, as despite the large number of $\langle 100 \rangle_{\beta}$ // BD textured fine grains, a greater area was occupied by non-textured grains. Qualitative examination of the EBSD reconstruction indicated the fine grains contained only $\langle 100 \rangle_{\beta}$ // BD texture. When compared with specimen 1.4, holistically a greater reduction in texture was achieved despite the large area of epitaxially grown horizontal grains indicated by the distribution and lower intensity of the pole figures.

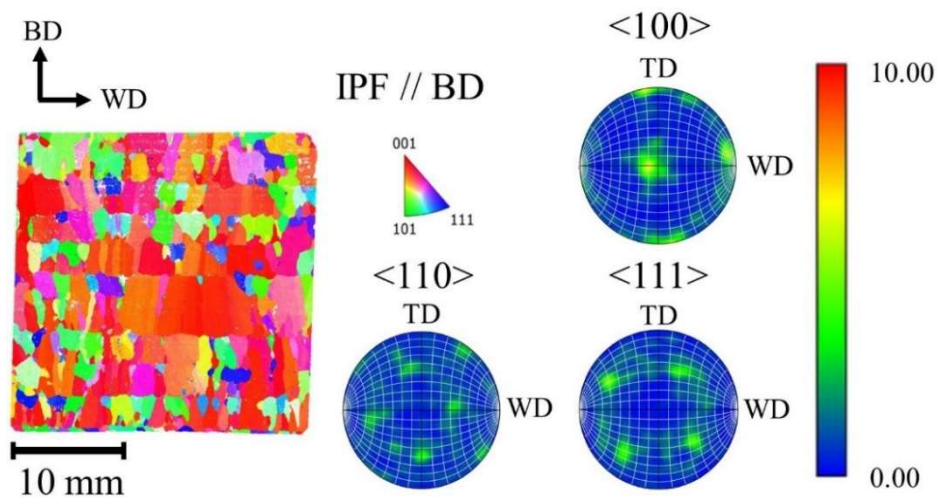


Figure 4-7: Prior- β grain reconstructed IPF map with respect to build direction (BD) and titanium cubic pole figures for Ti-6Al-4V specimen 1.4 ($22.22 \text{ J} \cdot \text{mm}^{-3}$).

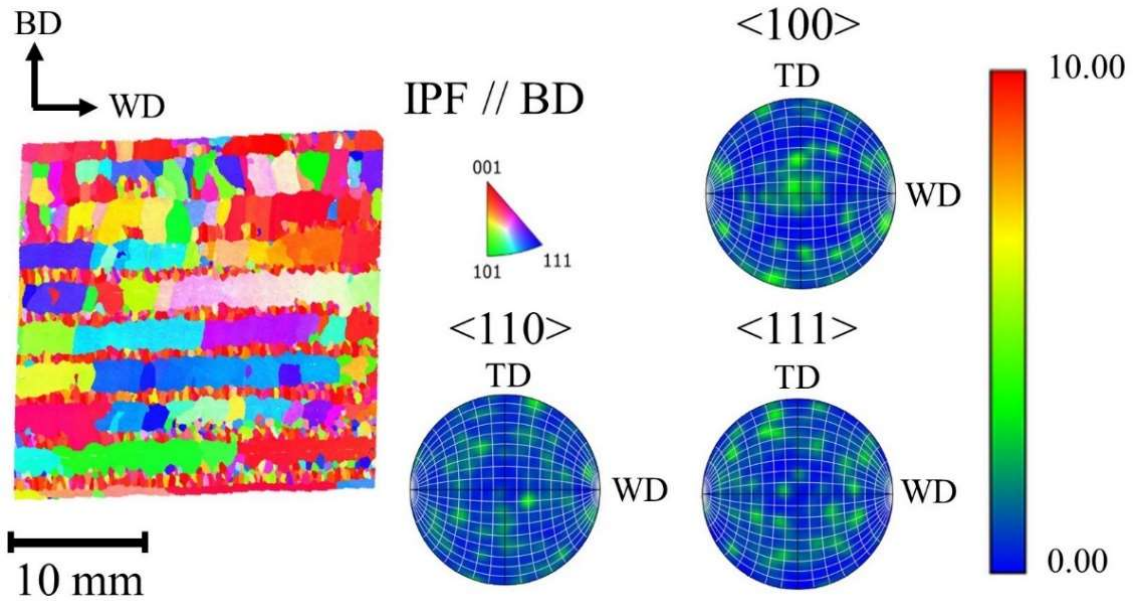


Figure 4-8: Prior- β grain reconstructed IPF map with respect to build direction (BD) and titanium cubic pole figures for Ti-6Al-4V specimen 1.5 ($19.96 \text{ J} \cdot \text{mm}^{-3}$).

Typically, additive manufacturing processes demonstrate textured epitaxial prior- β grain growth which follows the build direction due to the successive layer-by-layer remelting and maximum thermal gradient perpendicular to the solidification front in line with preferred crystal growth orientations [18,53–55]. Therefore, the deposition of horizontally orientated grains that exhibit minimal texture was intriguing and is not something previously reported in the deposition of single track Ti-6Al-4V WAAM. It was apparent that the large horizontal grains grow epitaxially, due to their relatively significant length and blocked the preferred $\langle 100 \rangle_{\beta} // \text{BD}$ orientated growth of the fine sandwich grains, whilst showing no preference to the build direction. Additionally, considering the IPF prior- β reconstructed maps with colouring with respect to the deposition direction (WD) and transverse direction (TD) (Figure 4-9), it can be determined that the horizontal grains showed no preference to either direction, which may also be observed in the pole figures. Therefore, these grains appear to have nucleated at random and receive a growth advantage in order to outcompete the fine $\langle 100 \rangle_{\beta} // \text{BD}$ orientated grains, which was likely a result of a change in the maximum thermal gradient from being orientated towards the BD, to the WD as SED was reduced. This is possible if the grain first nucleates at the rear of the melt pool and the curvature at this point is steep enough such that the solidification front becomes perpendicular with the deposition direction. Following the maximum thermal gradient at this point with the fastest

solidification rate [34], these grains out compete the preferentially orientated $\langle 100 \rangle_{\beta}$ // BD grains growing from the bottom of the melt pool surface to block their growth. The shape of the melt pool is thus impacting on the morphology of the grain structure and its texture. Despite this, it can be determined that the reduction in SED led to a greater amount of nucleation events, indicated by the increasing number of grains.

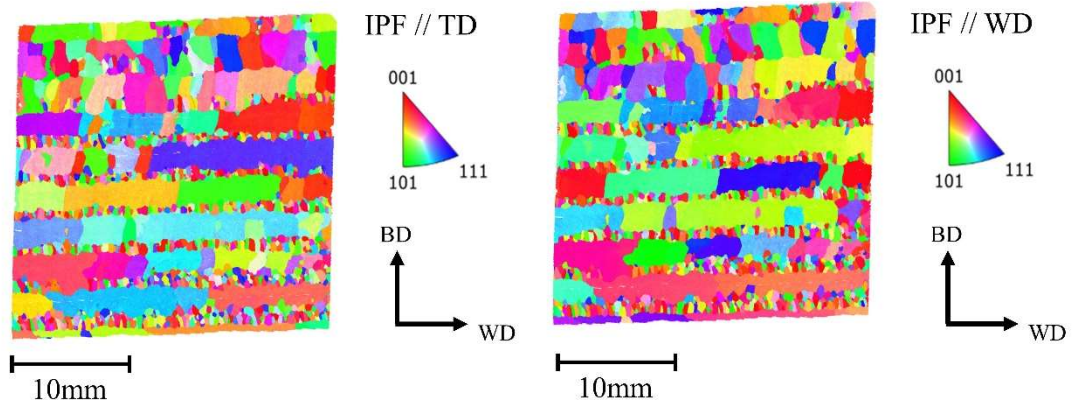


Figure 4-9: Prior- β grain reconstructed IPF of Ti-6Al-4V specimen 1.5 ($19.96 \text{ J} \cdot \text{mm}^{-3}$) a) with respect to the transverse direction b) with respect to deposition direction.

In relation to the base study [4], despite the reduction in TS and thus increase in heat input with an equivalent SED, the breakdown of the columnar prior- β grain structure occurred at a comparable rate. However, distinct morphological differences exist. The reduction in TS to reduce the solidification rate and make columnar-to-equiaxed more difficult to achieve as suggested by previous studies [27] did not manifest, although it was of a sufficient level to impact the mechanisms of grain growth. Whilst in the optimally refined specimen of the base study (Figure 4-3d), both grain morphology is refined and texture reduced, in this study, the optimally refined specimen 1.4 continued to exhibit a partially retained $\langle 100 \rangle_{\beta}$ // BD texture with the grain size and aspect ratio reduction. Furthermore, in specimen 1.5 the rows of fine equiaxed grains exhibited the same $\langle 100 \rangle_{\beta}$ // BD preferred orientation, whilst the large horizontal grains exhibited no preference to any direction that can be determined in this limited 2D data set. Despite the obvious morphological differences between specimen 1.5 and its base study SED counterpart, there was some convergence in the horizontal tilting of the grains, indicating the change in maximum thermal gradient with the SED reduction. The comparable rate of refinement indicates that the mechanism for CET was similar to that of the base study with regards to grain size and morphology, but the resultant texture was dependent on the heat input

as seen by others [56]. Therefore, it is unlikely that homogeneous nucleation ahead of the solidification front was the dominant growth mechanism as this would be reflected in the texture.

Due to the limited size of the deposited samples, it was not possible to extract tensile or fatigue specimens in such a way to be representative of various directions. However, microhardness measurements of all specimens of subset 1 were obtained to give an insight into mechanical performance [57] as the SED was reduced. The average hardness for specimens 1.1 – 1.5 was calculated to be $346.60 \text{ Hv} \pm 12.01$; $347.36 \text{ Hv} \pm 8.99$; $346.34 \text{ Hv} \pm 10.66$; $343.26 \text{ Hv} \pm 13.98$ and $340.00 \text{ Hv} \pm 18.84$ respectively. The variation in microhardness as the height of the specimen was traversed may be observed in Figure 4-10. In comparison to the base study [4], a similar trend was observed with a greater level of variation in the lower SED specimens. This can be explained by the variation in α morphologies observed within the prior- β grains as the SED reduced and melt pool geometry and cooling rate changed. Additionally, a ‘saw-tooth’ pattern was visible, which is associated to the microstructural coarsening that occurs during deposition and is well documented by Ho et al. [14]. The α morphology will have a significant effect on the mechanical properties [57–59] and, due to the ‘grain memory’ effect [42,60] when grain refinement is achieved by SED reduction, is best subjected to a β -anneal heat treatment to improve the α microstructure homogeneity whilst retaining the deposited prior- β grain morphology.

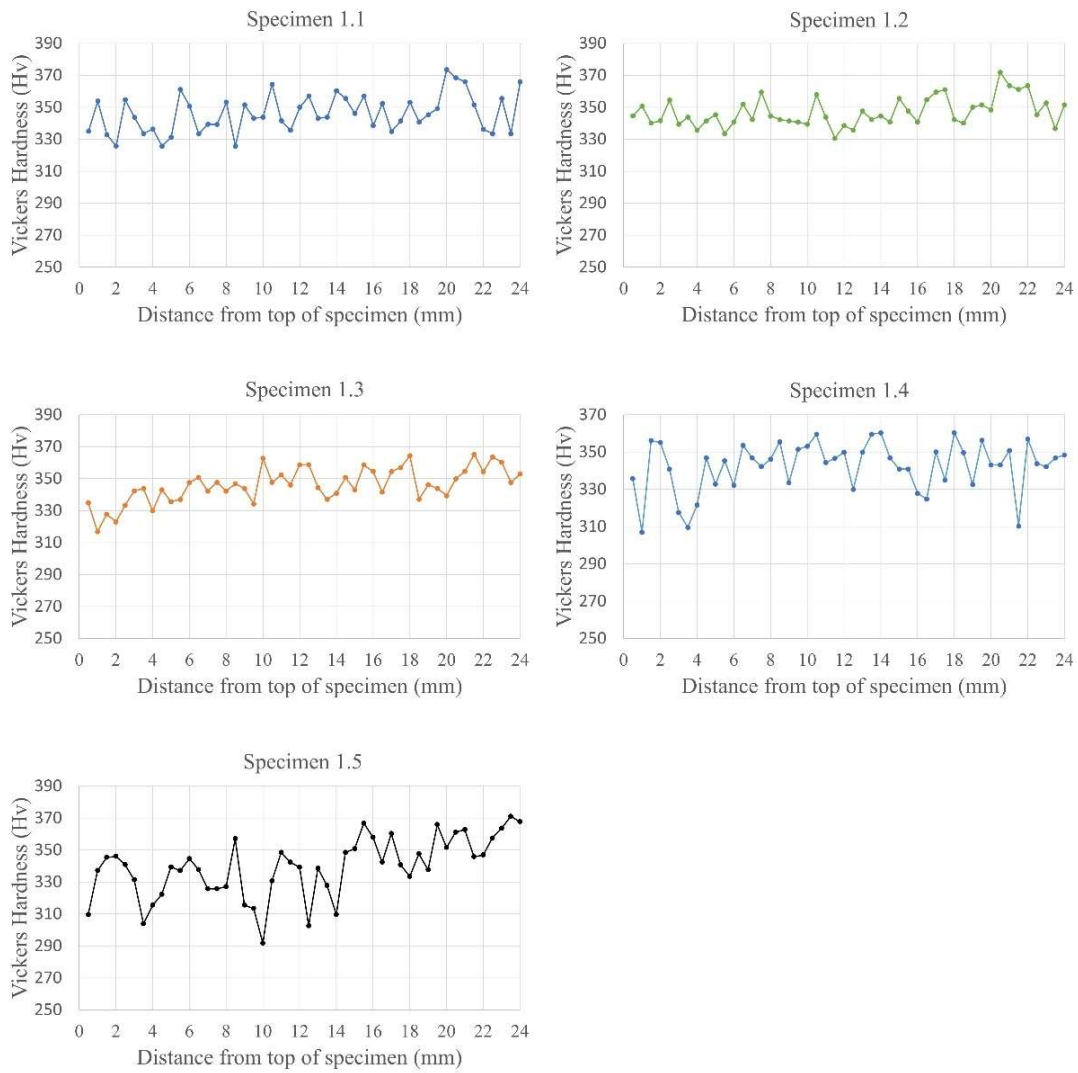


Figure 4-10: Microhardness ($HV_{0.3}$) measurements of Ti-6Al-4V specimens 1.1 – 1.5 - (1.1) $39.25 \text{ J} \cdot \text{mm}^{-3}$ (1.2) $29.67 \text{ J} \cdot \text{mm}^{-3}$ (1.3) $27.15 \text{ J} \cdot \text{mm}^{-3}$ (1.4) $22.22 \text{ J} \cdot \text{mm}^{-3}$ (1.5) $19.96 \text{ J} \cdot \text{mm}^{-3}$.

4.3.2 Increased Arc Current

The macrographs of the Ti-6Al-4V subset 2 specimens may be observed in Figure 4-11. During the deposition of this subset, the SED and TS were maintained against the base study [4], but an increased arc power and deposition rate implemented. This was conducted to understand whether SED is a definitive predictive measure of prior- β grain structure, irrespective of total arc energy. Qualitative analysis indicates that as SED was reduced a breakdown of the columnar prior- β grains occurred. However, in comparison to the base study and subset 1 of this study, the breakdown of columnar prior- β grains did not occur at the same rate. In subset 2, a columnar morphology dominated the prior- β grain structure at a SED of $37.83 \text{ J} \cdot \text{mm}^{-3}$, $30.29 \text{ J} \cdot \text{mm}^{-3}$ and $28.30 \text{ J} \cdot \text{mm}^{-3}$. Where

previously the optimally refined prior- β grain structure had been observed at an equivalent SED, in this subset when the SED dropped to 22.28 J.mm^{-3} , instead of an refined dominant structure, a mixed prior- β grain morphology may be observed, with several refined grains nucleated along the columnar grain boundaries. The highest level of prior- β grain refinement observed at an SED of 20.47 J.mm^{-3} , was significantly less refined than the equivalent optimal samples prior.

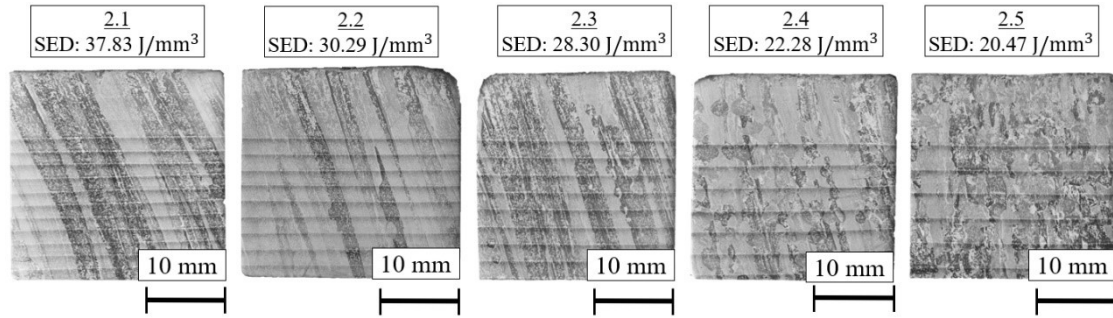
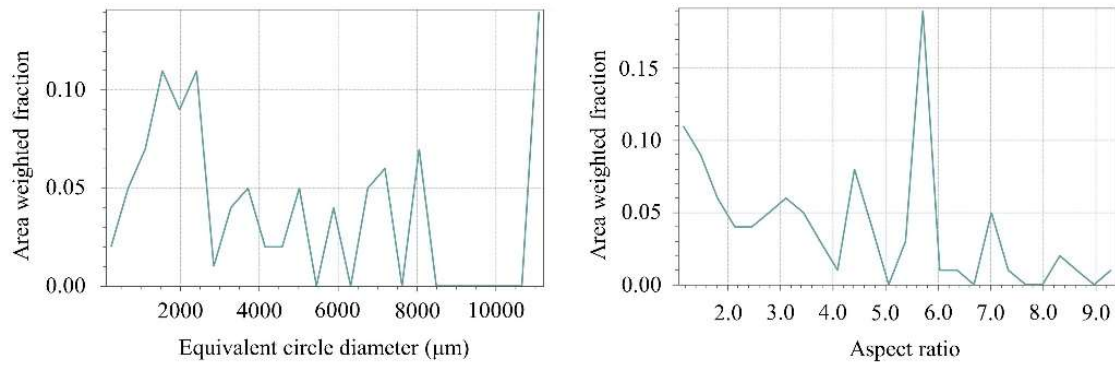


Figure 4-11: Light macrographs of etched longitudinal specimens of subset 2 demonstrating a breakdown in columnar grain structure of Ti-6Al-4V as SED is reduced from 37.83 J.mm^{-3} to 20.47 J.mm^{-3} . Note the lack of refinement for specimen 2.4 (22.28 J.mm^{-3}) as compared to the equivalent SED for subset 1 and base study.

Specimens 2.4. and 2.5 were selected for EBSD analysis, where the columnar prior- β structure began to breakdown. EBSD prior- β grain reconstruction allowed measurement of the grain size (equivalent circle diameter) and aspect ratio to indicate the level of refinement achieved. In specimen 2.4 a total of 467 grains were identified with a mean grain size of $935 \mu\text{m} \pm 40 \mu\text{m}$ and aspect ratio of 2.74 ± 0.09 . In specimen 2.5 a total of 599 grains were identified with a mean size of $919 \mu\text{m} \pm 34 \mu\text{m}$ and aspect ratio of 2.29 ± 0.05 . The grain size distribution throughout specimen 2.4 and 2.5 may be observed in Figure 4-12.

Specimen 2.4



Specimen 2.5

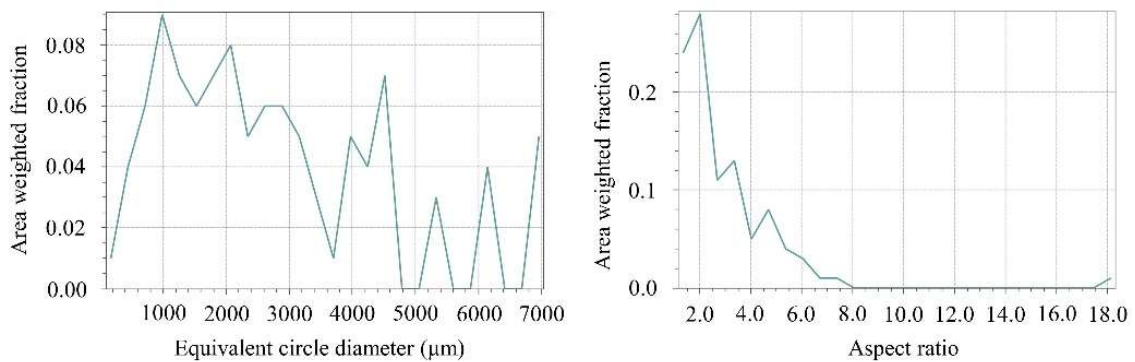


Figure 4-12: Grain size (L) and aspect ratio (R) distribution by area weighted fraction for Ti-6Al-4V specimens 2.4 ($22.28 \text{ J} \cdot \text{mm}^{-3}$) and 2.5 ($20.47 \text{ J} \cdot \text{mm}^{-3}$).

In specimen 2.4 it is clear that a large proportion of prior- β grains which exist $> 3000 \mu\text{m}$ dominated the majority of the sample, however, where refinement had occurred and equiaxed grains were present these have nucleated grains between $200 - 3000 \mu\text{m}$. This is also evident in the aspect ratio distribution where columnar grains between $5 - 6$ were dominant, then refined grains at < 2 . This differs wildly from the previous subset and base study, where the largest proportion of grains were $< 2000 \mu\text{m}$ as a consequence of prior- β refinement with aspect ratio dominated by < 2 . In comparison, for specimen 2.5 where a greater level of refinement has occurred, it is clear to see the grain structure was dominated by $< 3000 \mu\text{m}$ prior- β grains, however, this is not as refined as subset 1 or the base study, with a larger proportion of ‘big’ grains. It is clear that whilst the SED and travel speed remained consistent with the base study, the level of refinement achieved throughout specimens 2.1 – 2.5 had occurred at a slower rate, the cause of which is yet to be identified, but indicates that SED is not an outright predictor of prior- β grain structure.

Prior- β grain reconstructions with IPF colouring with respect to the build direction and standard titanium cubic pole figures may be observed in Figures 4-13 and 4-14 for specimens 2.4 and 2.5 respectively. Examination of the IPF map in Figure 4-13 aligns with the qualitative examination of the etched macroscopic image of specimen 2.4 (Figure 4-11). A strong $\langle 100 \rangle_\beta // \text{BD}$ texture was confirmed, with few non-textured refined grains present along the columnar grain boundaries. This morphology is more akin to the prior- β grain morphology of the 30.39 J.mm^{-3} and 28.48 J.mm^{-3} specimens of the base study. It was clear that for specimen 2.4, despite evidence of prior- β grain refinement with a reduction in SED, the growth mechanism continued to be dominated by a preferentially orientated and epitaxial growth mechanism. The strong texture of specimen 2.4 may be observed in the pole figures, where a strong intensity can be identified in relation to the $\langle 100 \rangle_\beta // \text{BD}$, with a similar maximum intensity to the columnar specimens observed in the base study (Figure 4-4). The reconstructed prior- β grain structure of specimen 2.5 may be observed Figure 4-14 which shares similar morphological characteristics to specimen 1.4 of subset 1. Despite the SED of specimen 2.5 (20.47 J.mm^{-3}) being lower than specimen 1.4 (22.22 J.mm^{-3}) and travel speed higher, the number of grains and their morphology are extremely similar.

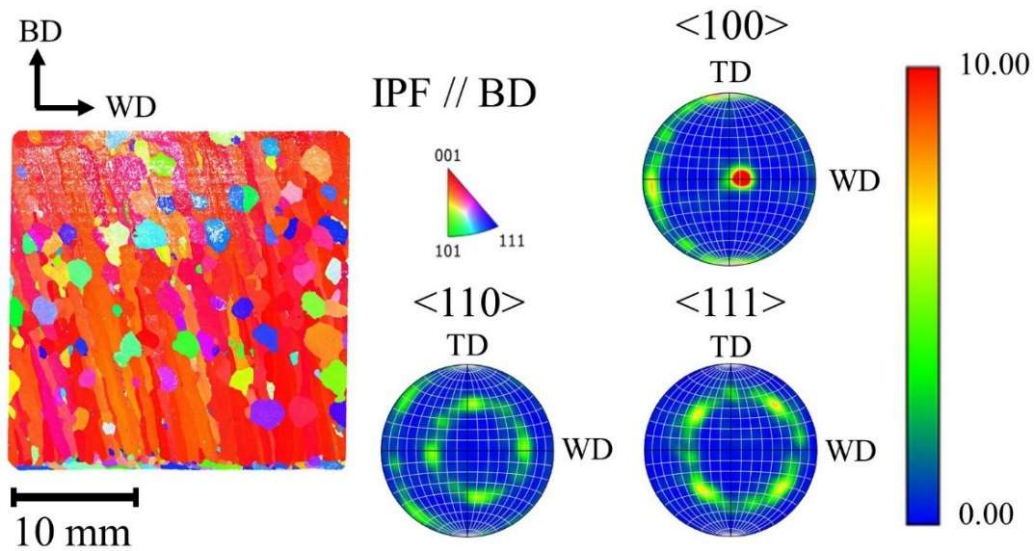


Figure 4-13: Prior- β grain reconstructed IPF map and titanium cubic pole figures for Ti-6Al-4V specimen 2.4 (22.28 J.mm^{-3}).

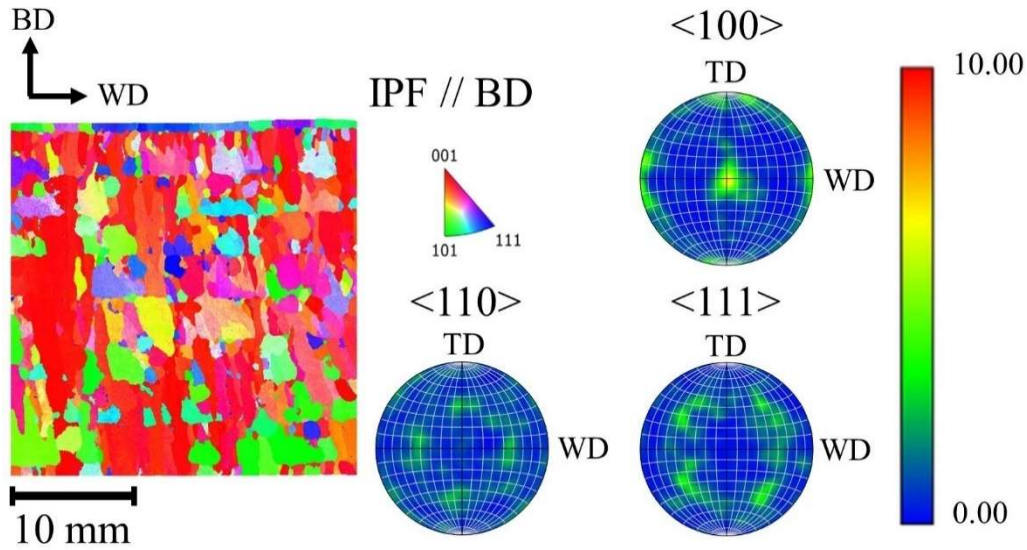


Figure 4-14: Prior- β grain reconstructed IPF map and titanium cubic pole figures for Ti-6Al-4V specimen 2.5 ($20.47 \text{ J} \cdot \text{mm}^{-3}$).

Analysis of the texture in the cubic pole figures demonstrated that whilst refinement did occur as SED reduced, there remains a strong $\langle 100 \rangle_{\beta} // \text{BD}$ texture in specimen 2.5, more so than in the morphologically similar specimen 1.4. This was clear when examining the IPF prior- β grain reconstructed map, where epitaxially columnar grains could be seen extending across multiple layers. Despite the equivalent SED and TS to the base study, the increase in arc energy supplied to the substrate led to prior- β refinement being more difficult to achieve. With increased arc energy it was expected that the thermal gradient during deposition may increase as a consequence of the increased heat input, thus preventing nucleation ahead of the solidification front, however, this was not the case. During deposition, measurement of the melt pool temperature was conducted using pyrometry and the thermal gradients calculated for subset 2 using the linear thermal gradient approximation by Bermingham et al. [27], whereby the melting temperature is subtracted from the average measured melt pool temperature and divided by the average layer height for the area of interest. Table 4-3 compares the linear thermal gradients of subset 2 with those of the equivalent SED in the base study [4]. As may be observed, when SED is maintained, despite the difference in arc power, the thermal gradients are equivalent, indicating that the SED determines the thermal gradient. With the difference in observed prior- β grain structure between subset 2 and the base study for equivalent SED and TS, it can be concluded that SED is not an outright predictor of grain structure during the deposition of Ti-6Al-4V during WAAM when considering the mechanism of grain refinement to be in terms of solidification rate and thermal gradient. Instead, similar

to subset 1, the prior- β grain morphology may be influenced by the change in melt pool shape, which was the only observable difference between subset 2 and the base study during deposition as a result of increased arc energy and change in WFS/TS ratio [38] which generated wider and taller deposited layers with a longer melt pool length.

Table 4-3: Linear thermal gradient approximation of the base study (Ti-6Al-4V) compared to subset 2 (Ti-6Al-4V)

Specimen	SED (J.mm ⁻³)	Thermal Gradient (°C.mm ⁻¹)	Specimen	SED (J.mm ⁻³)	Thermal Gradient (°C.mm ⁻¹)
BS 1.1	37.93	528.43 ± 34.75	2.1	37.83	558.69 ± 97.83
BS 1.2	30.39	351.12 ± 24.72	2.2	30.29	307.45 ± 57.44
BS 1.3	28.48	283.53 ± 43.71	2.3	28.30	250.30 ± 38.00
BS 1.4	22.28	207.83 ± 26.69	2.4	22.28	199.19 ± 34.80
BS 1.5	21.64	196.58 ± 27.06	2.5	20.47	211.81 ± 40.21

*Base study results reported in Wainwright et al. [4]

As previously mentioned, the limited deposition size only facilitated the measurement of microhardness. The average hardness for specimens 2.1 – 2.5 was determined to be 319.86 Hv ± 31.06; 313.18 Hv ± 26.44; 339.45 Hv ± 11.85; 320.53 Hv ± 23.97 and 334.46 Hv ± 16.68 respectively. As compared to subset 1 and the base study, there was a greater variation in microhardness measurements in each specimen from the top to the bottom of the deposit, as may be observed in Figure 4-15.

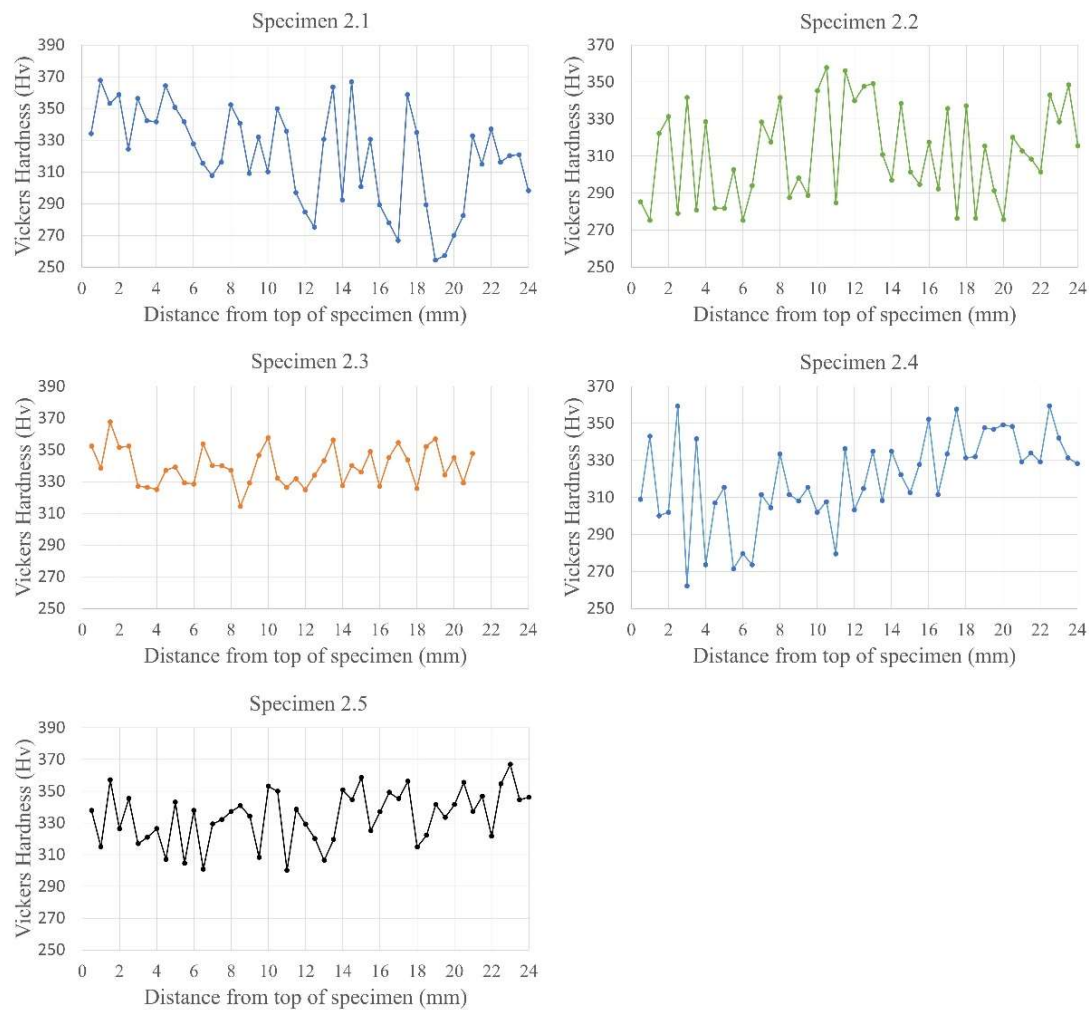


Figure 4-15: Microhardness ($HV_{0.3}$) measurements of Ti-6Al-4V specimens 2.1 – 2.5 - (2.1) $37.83 \text{ J} \cdot \text{mm}^{-3}$ (2.2) $30.29 \text{ J} \cdot \text{mm}^{-3}$ (2.3) $28.30 \text{ J} \cdot \text{mm}^{-3}$ (2.4) $22.28 \text{ J} \cdot \text{mm}^{-3}$ (2.5) $20.47 \text{ J} \cdot \text{mm}^{-3}$.

Conversely, a ‘softer’ microstructure was observed in the initial columnar specimens as compared to the lower SED specimens. Whilst further investigation is necessary to understand this phenomenon, as the primary focus of this study is the prior- β grain structure morphology, this was likely a result of an increase in heat input and associated change in cooling rate [56], which was more prominent in this subset as arc energy was increased when compared to the reduction in travel speed. Again, it was possible to observe the ‘saw-tooth’ pattern associated with the α coarsening as a consequence of multiple heat cycles [14].

4.3.3 Ti-6Al-2Sn-4Zr-2Mo Deposition

The macrographs of subset 3 are presented in Figure 4-16, the deposition conditions used were equivalent to the base study [4], with the exception of the feedstock material being

replaced with Ti-6Al-2Sn-4Zr-2Mo. The purpose of this subset was to increase the amount of potential constitutional supercooling as a consequence of the increased growth restriction factor of the additional alloying elements. In particular, the slow diffusion of molybdenum [19] to encourage nucleation ahead of the solidification front, and the effect of growth restriction elements limiting size of nucleated grains, allowing more grains to survive [19,61]. It was anticipated refinement would occur at a higher value of SED than that of the Ti-6Al-4V (which has less solute partitioning thus constitutional supercooling making it harder to achieve prior- β grain refinement). Obtained results indicated that the reduction in SED culminated in the refinement of the prior- β grain structure at an equivalent morphological rate as the base study Ti-6Al-4V. Columnar prior- β grains may be observed at 36.27 J.mm⁻³, before nucleation and growth of several refined grains, distributed throughout specimen 3.2 at 30.68 J.mm⁻³. As the SED was further reduced to 25.33 J.mm⁻³, the prior- β grain morphology appeared to contain fine columnar grains equally distributed with equiaxed grains to provide a mixed structure. Equivalent to the base study and subset 1, the optimal level of grain refinement can be found in specimen 3.4 at a SED of 22.33 J.mm⁻³. However, unlike the base study Ti-6Al-4V, evidence of several fine columnar grains may be identified. At 19.65 J.mm⁻³ the fine grain morphology was interrupted, with seemingly larger grains spanning across the direction of deposition and fine columnar like grains.

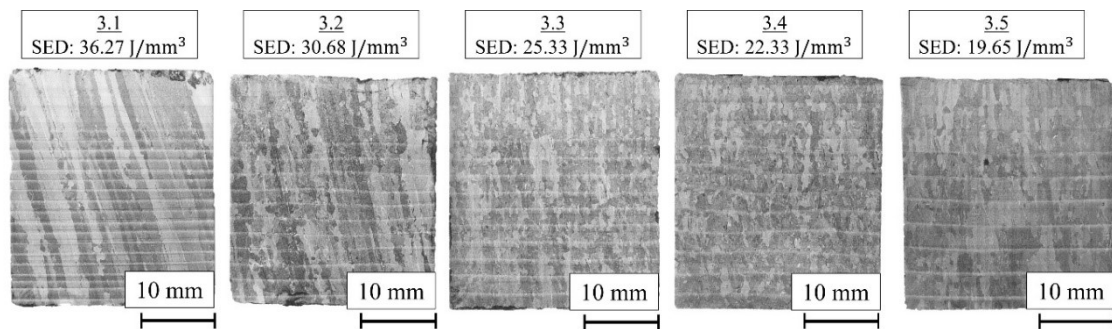


Figure 4-16: Light macrographs of etched longitudinal specimens of subset 3 demonstrating a breakdown in columnar grain structure of Ti-6Al-2Sn-4Zr-2Mo as SED is reduced from 36.27 J.mm⁻³ to 19.65 J.mm⁻³. Note an equivalent rate of prior- β grain structure breakdown from columnar to equiaxed as the base study during Ti-6Al-4V deposition.

To ensure that the Ti-6Al-2Sn-4Zr-2Mo feedstock specimens were not diluted by the Ti-6Al-4V substrate, X-EDS was conducted on each subset 3 specimen, at the bottom and top (1mm from the specimen edge) and middle of the specimen. The average alloy composition for each specimen measured by X-EDS at these points is detailed in Table 4-4. As may be observed there was no apparent dilution of the specimens with the Ti-

6Al-4V substrate. Additionally, Figure 4-17 demonstrates the change in alloy composition from the base of specimen 3.1 wall upwards. It may be observed that an almost instantaneous compositional change is achieved over less than 0.5 mm. The compositional gradient is dependent on the heat input and levels of remelting, thus time for diffusion and level of mixing, 1 – 2 mm gradients have been reported elsewhere [61]. Due to the additional 20 mm of ‘waste’ material first deposited and the results of the Ti-6Al-2Sn-4Zr-2Mo X-EDS, the Ti-5Al-5Mo-5V-3Cr feedstock specimens (subset 4) were also assumed to be clear from dilution.

Table 4-4: Composition of subset 3 (Ti-6Al-2Sn-4Zr-2Mo) specimens as measured by X-EDS across 3 test sites within each specimen

Specimen	Composition (wt %)					
	Ti	Al	Zr	Mo	Sn	V
3.1	81.74 ± 1.43	5.46 ± 0.11	4.02 ± 0.11	2.01 ± 0.05	2.34 ± 0.11	0.01 ± 0.01
3.2	85.27 ± 0.08	5.88 ± 0.01	4.25 ± 0.03	2.18 ± 0.04	2.36 ± 0.02	0.06 ± 0.02
3.3	85.37 ± 0.01	5.81 ± 0.01	4.29 ± 0.01	2.10 ± 0.03	2.39 ± 0.03	0.03 ± 0.01
3.4	85.36 ± 0.03	5.83 ± 0.01	4.19 ± 0.01	2.17 ± 0.04	2.40 ± 0.05	0.02 ± 0.01
3.5	85.42 ± 0.08	5.82 ± 0.01	4.22 ± 0.02	2.10 ± 0.04	2.39 ± 0.06	0.03 ± 0.01

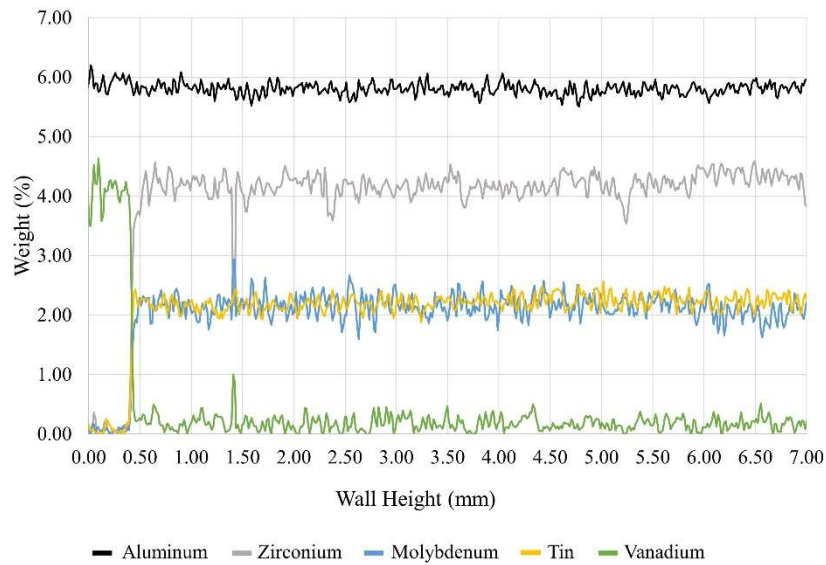


Figure 4-17: Composition of the Ti-6Al-2Sn-4Zr-2Mo wall deposited on Ti-6Al-4V substrate during deposition of specimen 3.1 ($36.27 \text{ J} \cdot \text{mm}^{-3}$). Note the lack of diffusion between the substrate and feedstock material and quick compositional change.

To characterise the deposition of this alloy in comparison to Ti-6Al-4V, all specimens were subjected to EBSD analysis. Post prior- β analysis, the grain size (equivalent circle

diameter) and aspect ratios were measured to quantify the level of prior- β grain refinement obtained. The grain size and aspect ratios in comparison to the base study are presented in Table 4-5. As may be ascertained, the size of the Ti-6Al-2Sn-4Zr-2Mo grains were considerably smaller than the Ti-6Al-4V, most noticeably for the high SED specimens. Whereas the Ti-6Al-4V demonstrated a gradual change in the refinement as observed by the number of grains, during the deposition of Ti-6Al-2Sn-4Zr-2Mo at specimen 3.3 the number of grains increased by more than double that of specimen 3.2. As expected the addition of the growth restriction from the Mo [19,61] led to a lower overall average grain size during the deposition of the Ti-6Al-2Sn-4Zr-2Mo as compared to the Ti-6Al-4V with equivalent deposition conditions, even for the columnar prior- β grain specimens. This has been seen with other growth restricting elements such as boron and yttrium when added to Ti-6Al-4V, due to their slow diffusion, thus reducing the width of columnar prior- β grains [30,31] during solidification. The level of refinement in terms of aspect ratio seemed similar and appeared to stabilise ~ 2.0 retaining some level of elongation.

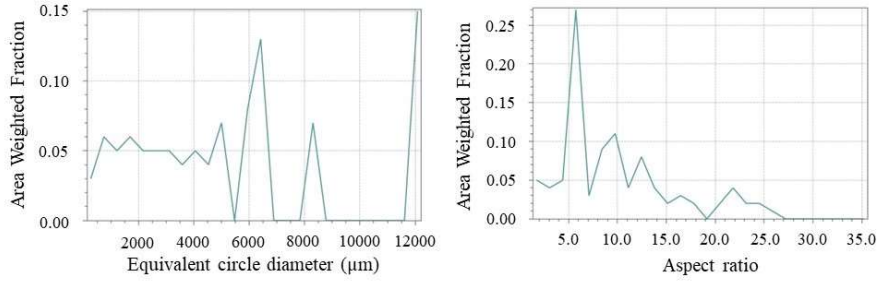
Table 4-5: Grain size and aspect ratio of base study (BS) [4] Ti-6Al-4V specimens versus Ti-6Al-2Sn-4Zr-2Mo specimens (3.1 – 3.5)

BS #	SED (J.mm ⁻³)	Grains	Grain size (μ m)	Aspect ratio	#	SED (J.mm ⁻³)	Grains	Grain size (μ m)	Aspect ratio
1	37.93	96	1797 $\pm$ 220	3.94 $\pm$ 0.26	3.1	36.27	469	843 $\pm$ 52.78	4.32 $\pm$ 0.19
2	30.39	313	1147 $\pm$ 64	3.69 $\pm$ 0.16	3.2	30.68	935	657 $\pm$ 20.42	2.63 $\pm$ 0.06
3	28.48	444	942 $\pm$ 46	2.33 $\pm$ 0.07	3.3	25.33	2134	535 $\pm$ 7.81	2.17 $\pm$ 0.02
4	22.28	710	821 $\pm$ 23	1.83 $\pm$ 0.03	3.4	22.33	1769	519 $\pm$ 7.12	2.11 $\pm$ 0.03
5	21.64	532	973 $\pm$ 34	2.47 $\pm$ 0.07	3.5	19.65	834	664 $\pm$ 18.45	2.53 $\pm$ 0.05

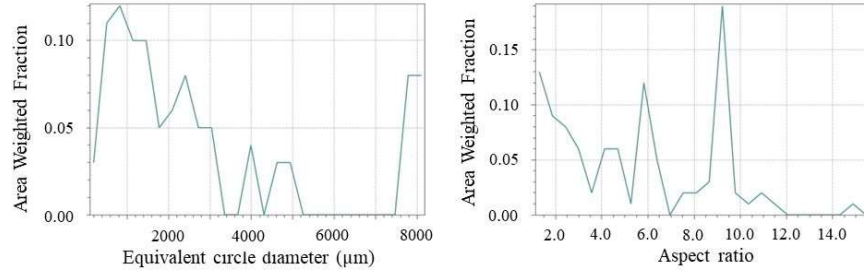
The grain size distributions for subset 3 are presented in Figure 4-18, with the rate of prior- β grain size and aspect ratio refinement as the SED is reduced being clear. At 36.27 J.mm⁻³, large > 6000 μ m grains dominated the specimen with large aspect ratios of > 5.0. As the SED reduced to 30.68 J.mm⁻³, grains < 3000 μ m began to dominate the grain structure, however, some large > 8000 μ m remained, whilst columnar grains continued to

dominate at > 8.0 aspect ratio. The prior- β grains show a large reduction in grain size from 25.33 J.mm^{-3} where $< 1000 \text{ }\mu\text{m}$ grains dominated with a dominant < 3.0 aspect ratio. Optimal refinement was achieved at 22.33 J.mm^{-3} where $< 1000 \text{ }\mu\text{m}$ prior- β grains dominated with a dominant < 2.0 aspect ratio. As the SED was further reduced to 19.65 J.mm^{-3} , similar to the base study, subset 1 and subset 2, the prior- β grains begin to enlarge with $> 1000 \text{ }\mu\text{m}$ manifesting.

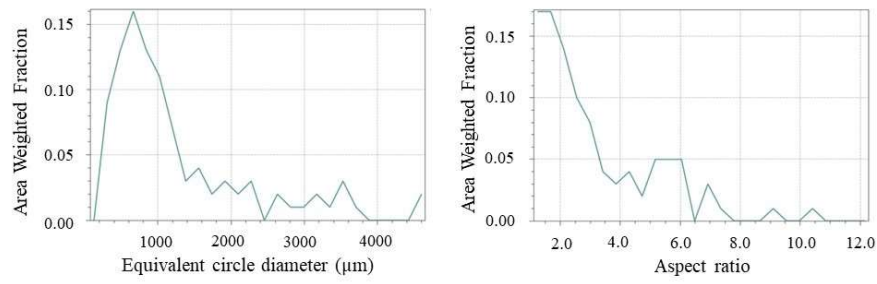
Specimen 3.1



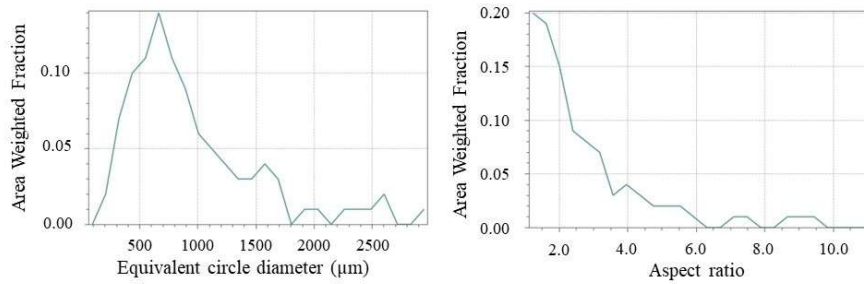
Specimen 3.2



Specimen 3.3



Specimen 3.4



Specimen 3.5

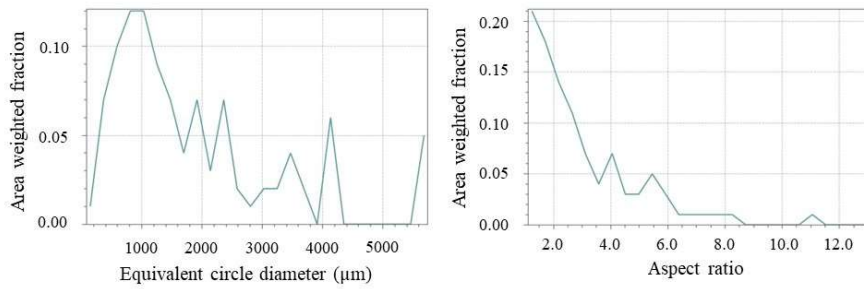


Figure 4-18: Prior-β grain size (L) and aspect ratio (R) distribution by area weighted fraction for Ti-6Al-2Sn-4Zr-2Mo specimens 3.1-3.5 at (3.1) $36.27 \text{ J} \cdot \text{mm}^{-3}$ (3.2) $30.68 \text{ J} \cdot \text{mm}^{-3}$ (3.3) $25.33 \text{ J} \cdot \text{mm}^{-3}$ (3.4) $22.33 \text{ J} \cdot \text{mm}^{-3}$ (3.5) $19.65 \text{ J} \cdot \text{mm}^{-3}$.

Due to the limited deposition size it was not possible to extract tensile or fatigue specimens to characterise mechanical performance with the reduction in SED and subsequent refinement of the prior- β grains. However, microhardness measurements of each specimen in subset 3 were conducted to give an indication of mechanical properties [57]. The average hardness of specimens 3.1 – 3.5 was found to be $331.30 \text{ Hv} \pm 27.69$; $326.76 \text{ Hv} \pm 26.98$; $350.53 \text{ Hv} \pm 17.84$; $338.79 \text{ Hv} \pm 20.34$ and $349.26 \text{ Hv} \pm 19.32$ respectively. The results of the microhardness testing may be observed in Figure 4-19. Note the typical variation of hardness as a consequence of the α coarsening during successive heating cycles near to the β -transus, forming a sawtooth pattern [14]. In comparison to the Ti-6Al-4V deposits, there appeared to be no particular change in the average microhardness of the specimen, however, there was more variation as compared to the base study. A significant number of peaks $370+$ Hv measurements may be observed as compared to the Ti-6Al-4V, which was likely a result of the secondary α microstructure that was present in the deposition of Ti-6Al-2Sn-4Zr-2Mo when compared to Ti-6Al-4V. This reduced the overall slip length and better prevented the movement of dislocations [61–64].

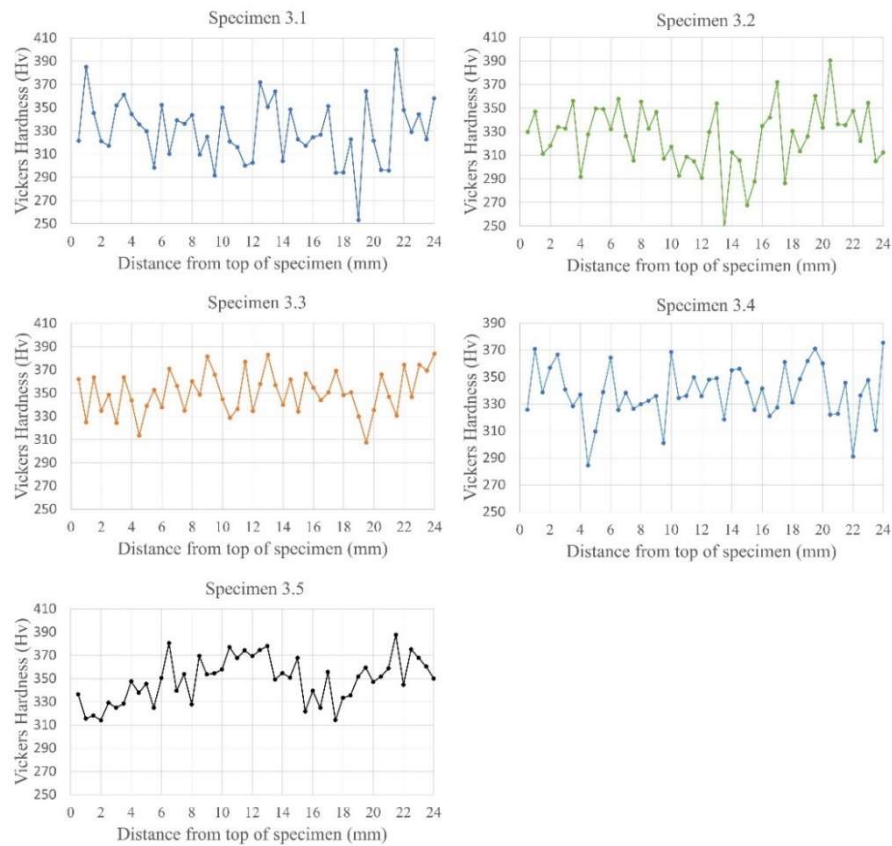


Figure 4-19: Microhardness (HV0.3) measurements of Ti-6Al-2Sn-4Zr-2Mo specimens 3.1 – 3.5 - (3.1) $36.27 \text{ J} \cdot \text{mm}^{-3}$ (3.2) $30.68 \text{ J} \cdot \text{mm}^{-3}$ (3.3) $25.33 \text{ J} \cdot \text{mm}^{-3}$ (3.4) $22.33 \text{ J} \cdot \text{mm}^{-3}$ (3.5) $19.65 \text{ J} \cdot \text{mm}^{-3}$.

A comparison of the α morphology between the columnar and optimally refined specimens from the Ti-6Al-4V deposition of the base study (SED's 37.93 J.mm^{-3} and 22.28 J.mm^{-3} respectively) and Ti-6Al-2Sn-4Zr-2Mo 3.1 and 3.4 specimens of this study (SED's 36.27 J.mm^{-3} and 22.33 J.mm^{-3} respectively) may be observed in Figure 4-20. In the back-scattered electron (BSE) images of the Ti-6Al-4V base study specimens the typical Widmanstätten α morphology may be observed [16] in both the columnar and refined cases. In the Ti-6Al-2Sn-4Zr-2Mo specimens in between the primary α lamellar, finer secondary α laths may be observed.

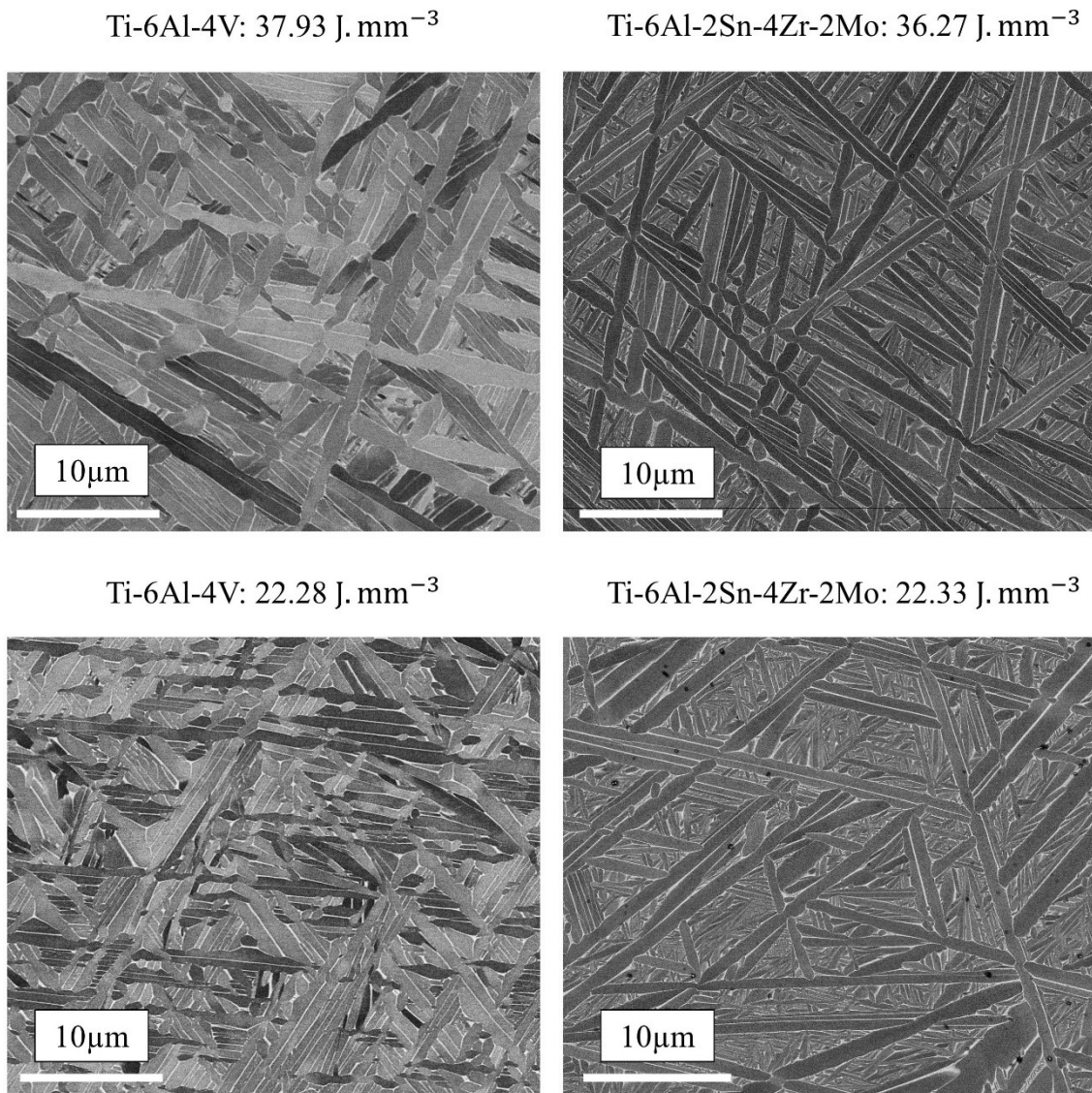


Figure 4-20: Back-scattered electron imaging comparing Ti-6Al-4V (L) and Ti-6Al-2Sn-4Zr-2Mo (R) α microstructure morphology for columnar (37.93 J.mm^{-3}) and optimally refined (22.28 J.mm^{-3}) prior- β grain specimens from the base study [4] and current study specimens 3.1 (36.27 J.mm^{-3}) and 3.4 (22.33 J.mm^{-3}) respectively.

In Figure 4-21 the reconstructed prior- β grain maps with IPF colouring relative to the building direction alongside their respective cubic pole figures may be observed. In alignment with the qualitative assessment of the etched specimens, it is clear that a breakdown in prior- β grain structure was achieved as SED was reduced. The rate of breakdown in comparison to the base study was almost identical, with equivalent columnar, mixed and equiaxed morphologies observed at similar SED levels. Conversely to the base study, the lowest SED specimen (3.5) showed evidence of much larger grains spanning across the height of the specimen as well as the width, similar to the prior- β grain structure observed in specimen 2.5. Additionally, there was a more noticeable difference in the size and number of columnar prior- β grains present in the subset. The additional growth restricting elements have prevented grain growth [19,61] and thus reduced the size of columnar grains rather than preventing their epitaxial growth. This effect translates also to the mixed and refined morphologies where much finer columnar prior- β grains can be observed. Despite the refinement in grain size, a stronger retention of the preferential $\langle 100 \rangle_{\beta}$ // BD texture was retained as compared to the Ti-6Al-4V base study (Figure 4-4). Specimens 3.1 (36.27 J.mm^{-3}) and 3.2 (30.68 J.mm^{-3}) demonstrated columnar grain growth and as expected this was reflected in the pole figures with a high intensity in the $\langle 100 \rangle_{\beta}$ // BD. The texture began to weaken as SED was reduced through specimens 3.3 (25.33 J.mm^{-3}) and 3.4 (22.33 J.mm^{-3}), however, a weak $\langle 100 \rangle_{\beta}$ // BD preferential orientation was retained. The similarity in the rate and morphology of the grain refinement as compared to the Ti-6Al-4V base study indicated that the mechanism of refinement between the studies was alike. The change in alloy constitution had little effect on impacting the rate of morphological change as it was expected to and refinement occurred at an equivalent SED. However, as previously mentioned an increase in the number of nucleation events, as may be observed by the increased number of grains for an equivalent area of measured material, was identified.

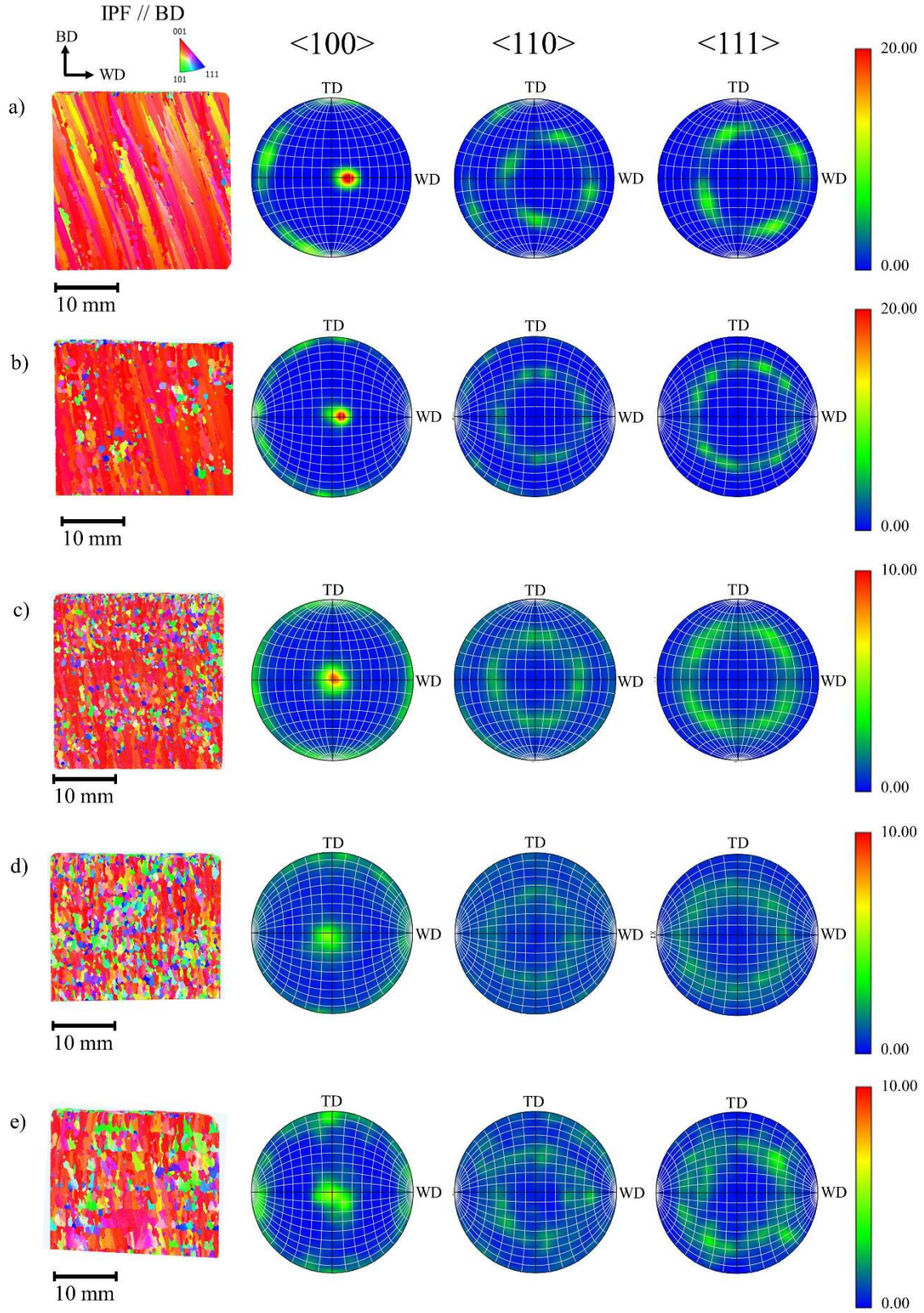


Figure 4-21: IPF prior- β reconstructions and cubic pole figures for Ti-6Al-2Sn-4Zr-2Mo specimens 3.1 – 3.5 a) 3.1 ($36.27 \text{ J} \cdot \text{mm}^{-3}$) b) 3.2 ($30.68 \text{ J} \cdot \text{mm}^{-3}$) c) 3.3 ($25.33 \text{ J} \cdot \text{mm}^{-3}$) d) 3.4 ($22.33 \text{ J} \cdot \text{mm}^{-3}$) e) 3.5 ($19.65 \text{ J} \cdot \text{mm}^{-3}$).

4.3.4 Ti-5Al-5Mo-5V-3Cr Deposition

The macrographs of the Ti-5Al-5Mo-5V-3Cr subset 4 specimens may be observed in Figure 4-22. The deposition conditions used were equivalent to those of the Ti-6Al-4V base study, with the exception of the wire feedstock material. Whilst this alloy differs from Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo as it exists as a metastable β alloy, it was expected to provide the greatest amount of constitutional supercooling and achieve refinement at comparatively higher values of SED. As may be observed in Figure 4-22, minimal grain refinement occurred in this subset, with columnar β grains dominating the entire specimen area. When the SED was reduced to $19.13 \text{ J} \cdot \text{mm}^{-3}$ in specimen 4.5, a small amount of refined grains began to appear in between the columnar grain boundaries. There was a distinctive contrast transition in the bottom of material to the top, this was a consequence of α precipitation during the successive heat cycles during deposition. Due to the overly dominant columnar β grain structure, EBSD was not performed on this subset.

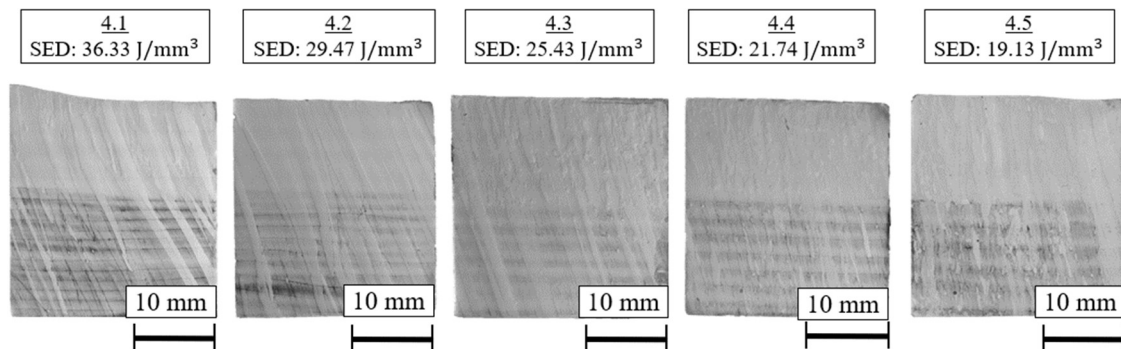


Figure 4-22: Light macrographs of etched longitudinal specimens of subset 4 demonstrating minimal breakdown in columnar β grain structure of Ti-5Al-5Mo-5V-3Cr as SED is reduced from $36.33 \text{ J} \cdot \text{mm}^{-3}$ to $19.13 \text{ J} \cdot \text{mm}^{-3}$. Note a distinct lack of β grain refinement.

During microhardness testing the effect of α precipitation became more noticeable as the SED was reduced. This was a consequence of the increased layer height which prevented less of the material from being remelted, leading to a less homogenous α microstructure when compared to the high SED which had a close spacing between banding. Further investigation is required to quantify this effect, however, considering Figure 4-23, the microhardness tests showed a larger level of variation existed towards the α precipitated region as the SED was reduced. A previous study by Cabellero et al. [65], demonstrated this effect, however, the α precipitated region demonstrated significantly higher hardness that was not captured in the current study. This was likely a consequence of less α

precipitation being present in the current study due to a lower heat input and difference in cooling rate.

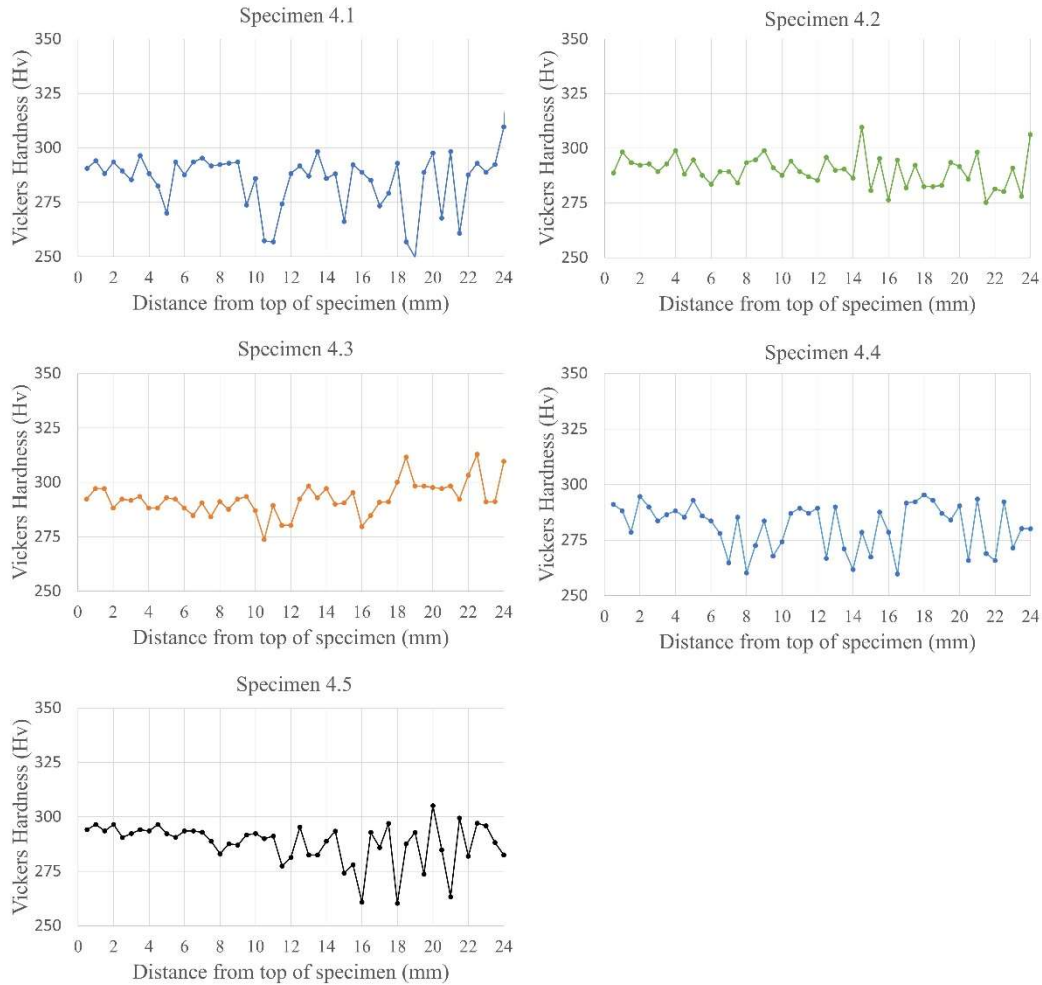


Figure 4-23: Microhardness ($HV_{0.3}$) measurements of Ti-5Al-5Mo-5V-3Cr specimens 4.1 – 4.5 - (4.1) 36.33 J.mm^{-3} (4.2) 29.47 J.mm^{-3} (4.3) 25.43 J.mm^{-3} (4.4) 21.74 J.mm^{-3} (4.5) 19.13 J.mm^{-3} .

The prior- β and β grain structures observed in subset 3 and 4 are of particular importance for identifying the underlying mechanism behind prior- β grain refinement, following the lack of refinement identified in subset 2 (where SED was replicated for a differing arc power to the base study) indicating SED was not a predictor of β grain structure. The equivalent rate of morphological deterioration in the Ti-6Al-2Sn-4Zr-2Mo and lack of refinement in Ti-5Al-5Mo-5V-3Cr grain structures demonstrated that the refinement mechanism was not achieved via a conventional columnar-to-equiaxed response. That is, the introduction of alloying elements that act as growth restricting elements and increase the level of constitutional supercooling [18,19,61], in particular the slow diffusion of molybdenum which provides greater segregation from titanium, increasing the available

constitutional supercooling thus opportunity for nucleation ahead of the solidification front. It was expected that refinement should occur at a higher SED to the base study, however, there was a limited effect observed. Whilst the size of the refined grains visibly reduced, inferring a great quantity of nucleation events, in subset 3 the additional theoretical constitutional supercooling did not impact the rate of the grain structure refinement at equivalent SED values, i.e. columnar, mixed or refined. In the case of subset 4, the opposite appears to have occurred, with refinement being harder to achieve, despite having the largest theoretical constitutional supercooling. Therefore, the refinement mechanism cannot only have been a direct result of promoting nucleation within the melt pool ahead of the solidification front. Instead, similar to the previous subsets and the base study, there was a difference in the melt pool geometry, which may also be a contributing factor that is noticeable in other studies [25,46].

4.3.5 Prior- β Grain Refinement Mechanism

As demonstrated by the results of this study, the mechanism of grain refinement does not appear directly linked to nucleation ahead of the solidification front to block epitaxial growth [27] and instead appears seemingly related to the melt pool geometry and curvature of the solidification front. This provides significant challenges with respect to experimental observation. However, it is possible to make assumptions based on available process monitoring techniques. Taking into account the ovular nature of the melt pool [66], it is possible to consider the length/depth (L/D) ratio in the longitudinal plane to measure the solidification front curvature by proxy. This must be done via process monitoring during deposition, as it is not possible to observe the solidification front post deposition in a deposit of a single alloy constitution [27]. Utilising the processing camera (mounted perpendicular to the deposition direction), identification of the melt pool length was possible and physical measurements of layer height were taken during deposition, to provide a proxy of rear melt pool curvature. Melt pool measurements were taken for all specimens across 3 randomly selected layers, at 3 randomly selected points. Little variation was seen, deeming the process was stable. An example of melt pool length measurement may be observed in Figure 4-24 of a randomly selected layer of subset 1. L/D ratios of all specimens in this study, also including those of the base study by Wainwright et al [4] were recorded.

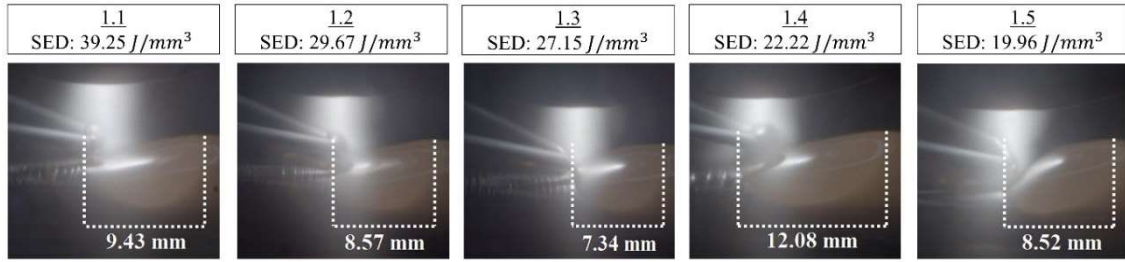


Figure 4-24: Melt pool length measurements of Ti-6Al-4V specimens 1.1 – 1.5 taken at randomly selected layers within final 30 mm of deposited material. Note: due to the number of melt pool length measurements, for conciseness and the readers benefit only one image is presented from each specimen of subset 1. The corresponding layers for each specimen are as follows: 1.1 – L32, 1.2 – L23, 1.3 – L27, 1.4 – L18, 1.5 – L20.

The L/D ratio of all specimens deposited in this study, including those of the base study by Wainwright et al. [4] may be observed in Table 4-6.

Table 4-6: L/D ratios of all titanium alloy specimens deposited including those of the base study (BS) [4] (Ti-6Al-4V – subsets 1,2 and BS, Ti-6Al-2Sn-4Zr-2Mo – subset 3 and Ti-5Al-5Mo-5V-3Cr – subset 4)

ID #	SED (J.mm ⁻³)	L/D ratio	ID #	SED (J.mm ⁻³)	L/D ratio
1.1	39.25	7.32 ± 0.06	2.1	37.83	11.41 ± 0.21
1.2	29.67	5.02 ± 0.11	2.2	30.29	8.96 ± 0.19
1.3	27.15	3.62 ± 0.04	2.3	28.30	7.75 ± 0.17
1.4	22.22	4.44 ± 0.07	2.4	22.28	5.61 ± 0.08
1.5	19.96	2.75 ± 0.05	2.5	20.47	5.58 ± 0.07

3.1	36.27	10.01 ± 0.34	4.1	36.33	11.68 ± 0.60
3.2	30.68	6.48 ± 0.22	4.2	29.47	9.52 ± 0.21
3.3	25.33	5.93 ± 0.10	4.3	25.43	8.22 ± 0.18
3.4	22.33	5.40 ± 0.09	4.4	21.74	7.41 ± 0.45
3.5	19.65	4.72 ± 0.07	4.5	19.13	6.69 ± 0.12

BS 1	37.93	8.98 ± 0.31
BS 2	30.39	6.99 ± 0.09
BS 3	28.48	4.83 ± 0.06
BS 4	22.28	4.18 ± 0.04
BS 5	21.64	3.26 ± 0.04

It may be observed that the L/D ratio decreased, indicating an increase in the curvature at the solidification front, as the SED was reduced. Primarily, this was driven by an increase in the layer height as the WFS/TS ratio was increased, which has been demonstrated to alter bead geometry accordingly [38], rather than through a significant reduction in melt

pool length. It may also be noted that the SED and L/D were independent of one another, therefore, confirming why different prior- β and β grain structures may be observed for equivalent SED. When considering the macrographs of all samples (including the base study) inclusive of their L/D ratios in Figure 4-25, it is clear that a distinct relationship between L/D ratio and β grain structure existed in the as-deposited condition. A L/D ratio of > 6 provides a columnar grain structure, < 6 provides a mixed structure, ~ 4 provides an optimal level of β grain refinement and < 4 the grain structure begins to tilt in favour of the deposition direction. This implies that a physical mechanical response based on the curvature of the solidification is responsible for the grain refinement of titanium alloys deposited with WAAM. This accounts for seemingly erroneous results such as those in subset 1, where during analysis of specimen 1.3 (27.15 J.mm^{-3}), horizontally tilted grains had appeared before the optimally refined specimen 1.4 which had a lower SED, this occurred due to a L/D of 3.78 in specimen 1.3 as opposed to an L/D of 4.28 in specimen 1.4. Additionally, this can explain the lack of refinement of the Ti-5Al-5Mo-5V-3Cr specimens, due to the thermophysical properties [65] of the alloy significantly increasing the melt pool length in subset 4. The lowest recorded L/D was 6.69 in specimen 4.5, despite having the lowest SED. However, specimen 4.5 showed a mixed β grain morphology dominated by columnar grains with few refined grains nucleated at the grain boundaries, equivalent to Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo of similar L/D ratios. Therefore, it can be determined that a primary factor behind grain refinement of β grains during solidification of titanium alloys is the shape of the melt pool during solidification.

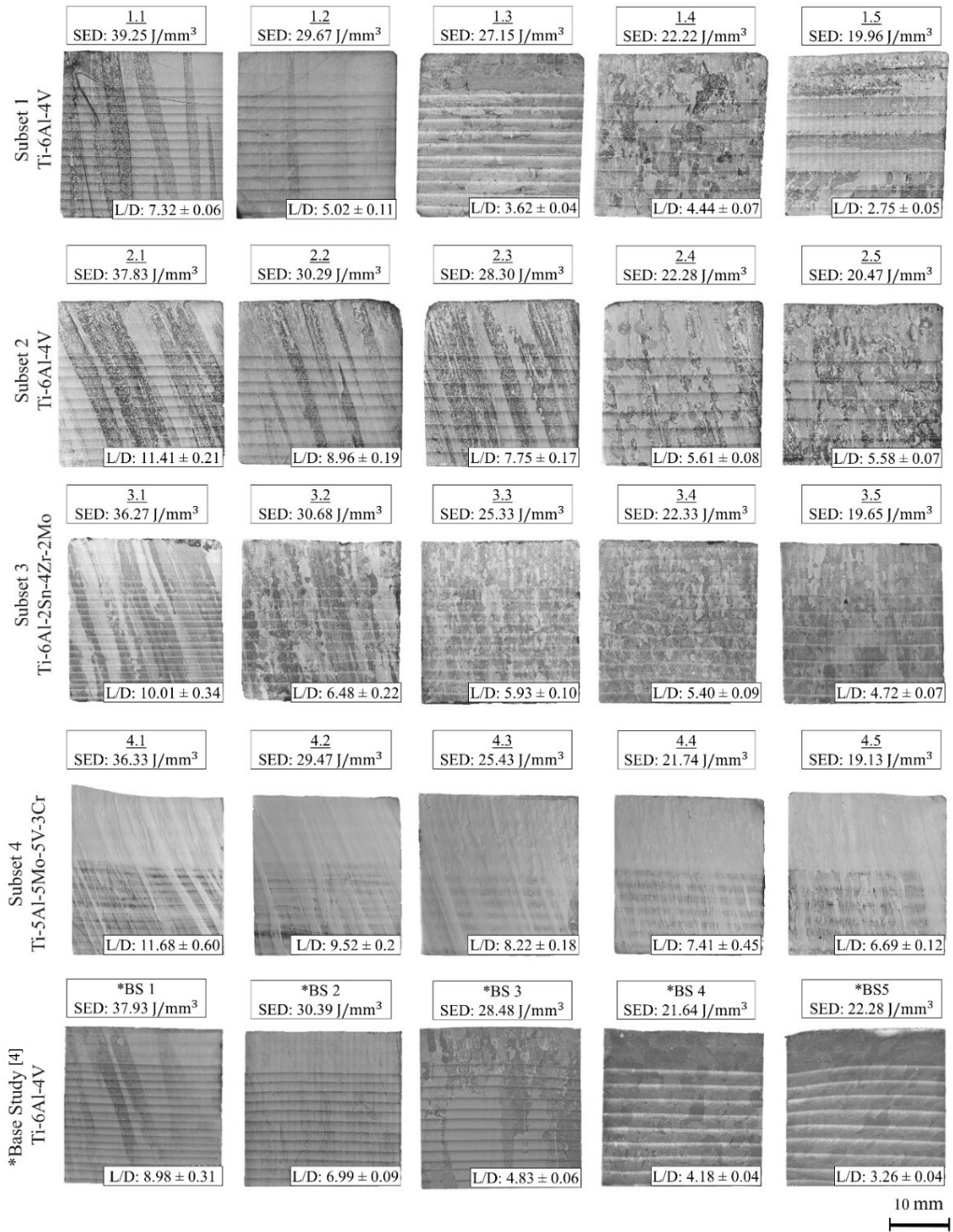


Figure 4-25: Light macrographs of etched macroscopic images of subset 1 – 4 and base study by Wainwright et al. [4], demonstrating the relationship between L/D ratio and prior- β and metastable β grain refinement. Note that > 6 forms a columnar dominant grain structure, < 6 a mixed morphology, ~ 4 an optimal refinement and < 4 tilting of the grains to the deposition direction and horizontal growth.

With the mechanism of refinement seemingly unrelated to the traditional columnar-to-equiaxed transition of nucleation ahead of the solidification front, further investigation of the EBSD reconstructions was conducted, with particular emphasis on the grain boundary misorientations of the prior- β grains in specimens; 1.4 and 1.5; 2.4 and 2.5; 3.1 – 3.5 and further analysis of the results of the base study [4]. Should nucleation ahead of the solidification front occur such that it provides a fully equiaxed grain structure, the misorientations between the prior- β grains would be random in nature and fit the Mackenzie distribution [67,68], a well-known probability plot associated with random misorientations in cubic phases.

Consideration of the prior- β grain boundary misorientations for specimens 1.4 and 1.5 demonstrated in Figure 4-26 that this did not occur. Both specimens retained a partial $\langle 100 \rangle_{\beta}$ // BD texture, therefore were not expected to fully fit the Mackenzie distribution and this was confirmed by the presence of the low angle grain boundaries (LAGB) $< 10^{\circ}$. When the L/D was lowest, specimen 1.5 showed more propensity to fit the Mackenzie distribution, yet still minimal. Instead a small peak of $\sim 51^{\circ}$ and large peak of $\sim 60^{\circ}$ was evident in addition to the $< 10^{\circ}$ LAGB. When L/D was lowest in subset 1, a greater volume of $\sim 60^{\circ}$ grain misorientations may be observed over LAGB. In specimens 2.4 and 2.5 a LAGB dominant misorientation distribution was expected due to the heavily epitaxial and strong $\langle 100 \rangle_{\beta}$ // BD texture, and as may be observed in Figure 4-26, refinement had only begun to occur rather than being optimal. The misorientations show a similar trend to those of subset 1. In both specimens 2.4 and 2.5, LAGB $< 10^{\circ}$ dominated the prior- β grain structure as expected by the large proportion of $\langle 100 \rangle_{\beta}$ // BD grains, however a small fraction of $\sim 60^{\circ}$ grain boundary misorientations began to appear.

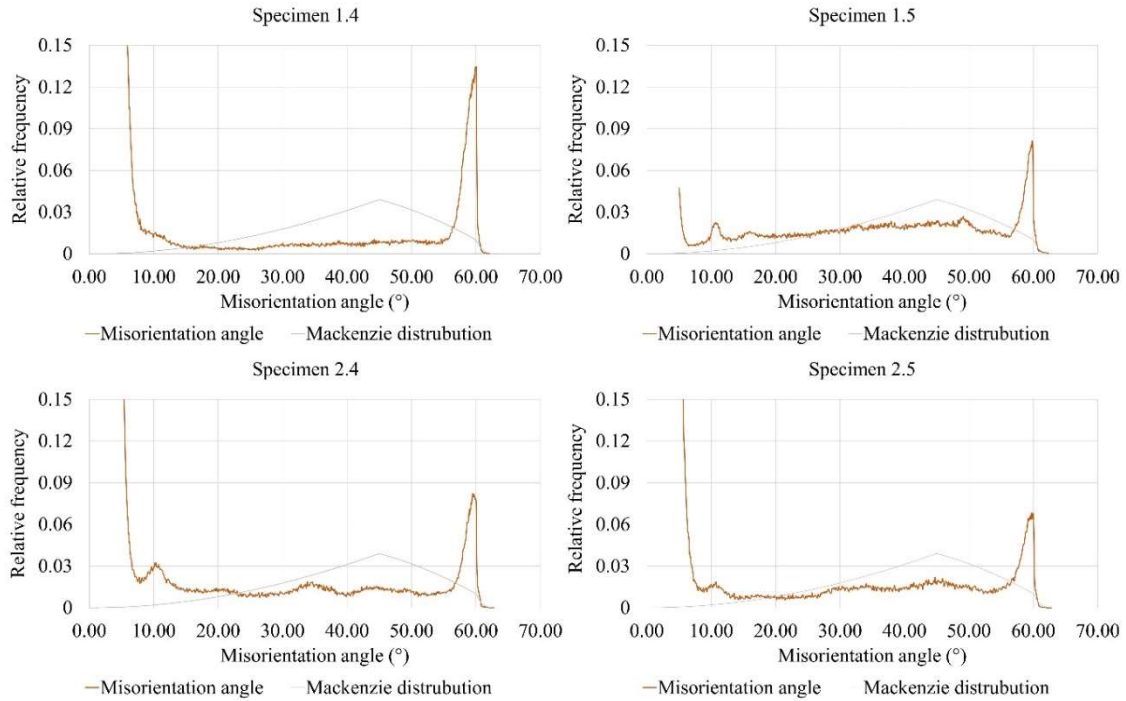


Figure 4-26: Prior- β grain boundary misorientations for Ti-6Al-4V specimens 1.4 and 1.5 ($22.22 \text{ J} \cdot \text{mm}^{-3}$ and $19.96 \text{ J} \cdot \text{mm}^{-3}$ respectively) and specimens 2.4 and 2.5 ($22.28 \text{ J} \cdot \text{mm}^{-3}$ and $20.47 \text{ J} \cdot \text{mm}^{-3}$ respectively). Note the retention of the $\langle 100 \rangle_{\beta} // \text{BD}$ with $\text{LAGB} < 10^\circ$, however, dominant grain boundary misorientations at primarily 60° and increase of 51° in some cases.

A better understanding of the prior- β grain boundary misorientation evolution was possible through the analysis of the subset 3 specimens, where all samples were fully characterised by EBSD. The evolution of the prior- β grain boundary misorientations from specimen 3.1 – 3.5, as the L/D reduced, may be observed in Figure 4-27. As the SED and L/D was reduced, the $\text{LAGB} < 10^\circ$ which dominated the misorientation distribution in the specimens successively become less dominant and were ultimately replaced by the $\sim 51^\circ$ and 60° grain boundary misorientation. Unlike the samples deposited in Ti-6Al-4V, the misorientation distribution better followed the Mackenzie distribution, indicating that some nucleation ahead of the solidification had occurred. This can be explained by the increased level of growth restriction as a consequence of the molybdenum providing a greater constitutional supercooling [18,19,61] and reduction in thermal gradient as SED was reduced [4,27] allowing β grains to solidify ahead of the solidification front. Therefore, the reduction in SED was contributing a minor role in prior- β grain refinement. However, the dominant prior- β grain boundary misorientations were associated with the $\sim 51^\circ$ and $\sim 60^\circ$ peaks. The 51° misorientations formed around $\langle 100 \rangle_{\beta}$, whilst the more dominant 60° peak formed around $\langle 111 \rangle_{\beta}$, these rotations correspond to known titanium

β phase twinning systems in body centred cubic metals of $\{332\}_{\beta} \langle 113 \rangle_{\beta}$ and $\{112\}_{\beta} \langle 111 \rangle_{\beta}$ respectively [69,70].

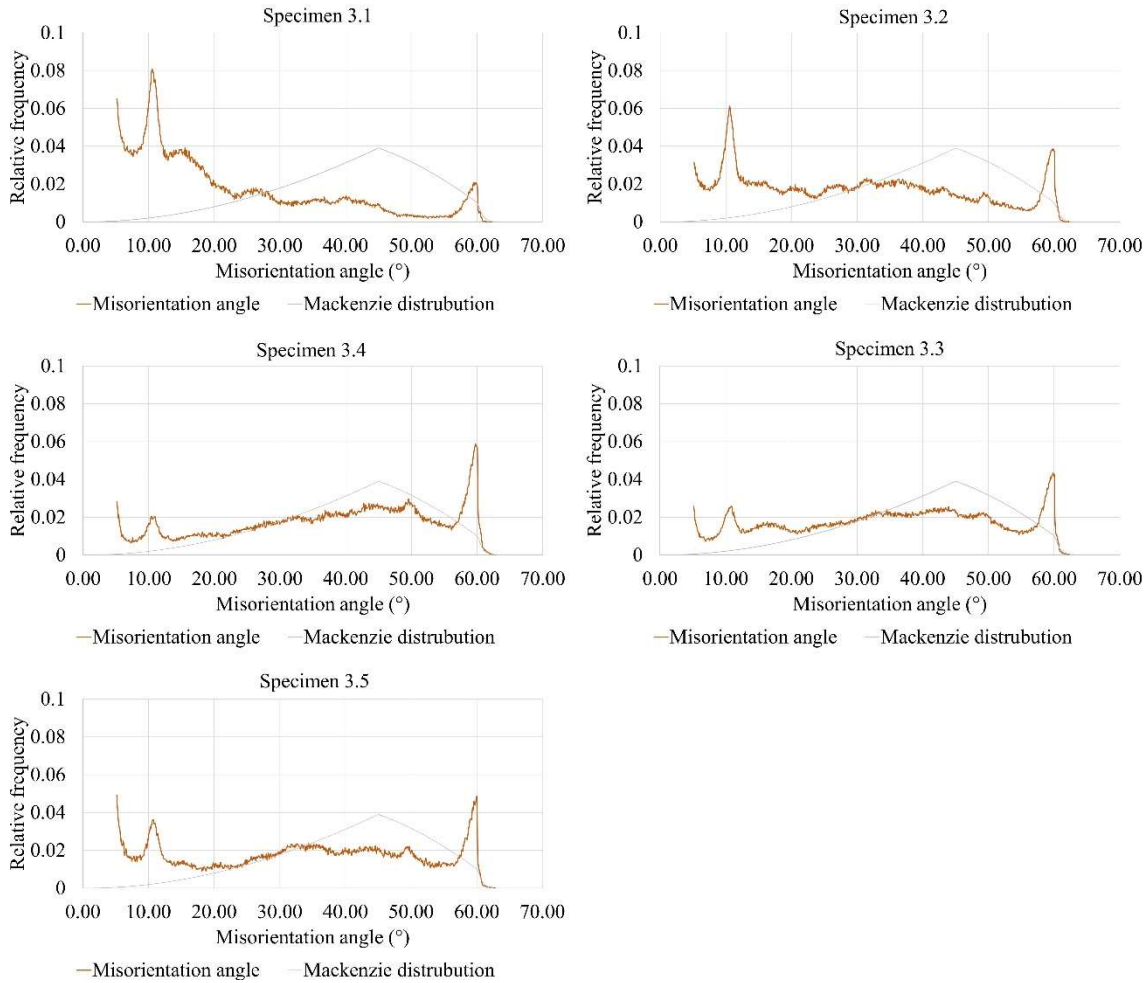


Figure 4-27: Prior- β grain boundary misorientations for specimen 3.1 – 3.5 deposited with Ti-6Al-2Sn-4Zr-2Mo ($36.27 \text{ J} \cdot \text{mm}^{-3}$, $30.68 \text{ J} \cdot \text{mm}^{-3}$, $25.33 \text{ J} \cdot \text{mm}^{-3}$, $22.33 \text{ J} \cdot \text{mm}^{-3}$, $19.65 \text{ J} \cdot \text{mm}^{-3}$). Note the evolution from LAGB $< 10^\circ$ towards the Mackenzie distribution, however, dominated in 51° and 60° .

The $51^\circ \langle 110 \rangle_{\beta}$ and $60^\circ \langle 111 \rangle_{\beta}$ misorientations are visualised in Figure 4-28 presented alongside their respective IPF // BD prior- β reconstruction maps for the Ti-6Al-2Sn-4Zr-2Mo at the highest SED ($36.27 \text{ J} \cdot \text{mm}^{-3}$) and L/D (10.01) and optimal SED ($22.33 \text{ J} \cdot \text{mm}^{-3}$) and L/D (5.40) where optimal refinement occurred, using the special boundaries feature of AztecCrystal. To allow for reconstruction errors during EBSD, a $\pm 5^\circ$ deviation from the twin orientations was taken into account. At a high value of SED, where the columnar epitaxial prior- β grains developed, a small contingency of refined grains may be observed. Consideration of the twin misorientation map illustrates that these refined grains contained a minimum of 1 twin boundary. When the SED was reduced along with

L/D ratio, a large proportion of refined grains are exhibited. Consideration of the twin maps for this sample are almost entirely dominated by these twin boundaries, confirming the primary source of refinement to be dendrite twinning during solidification.

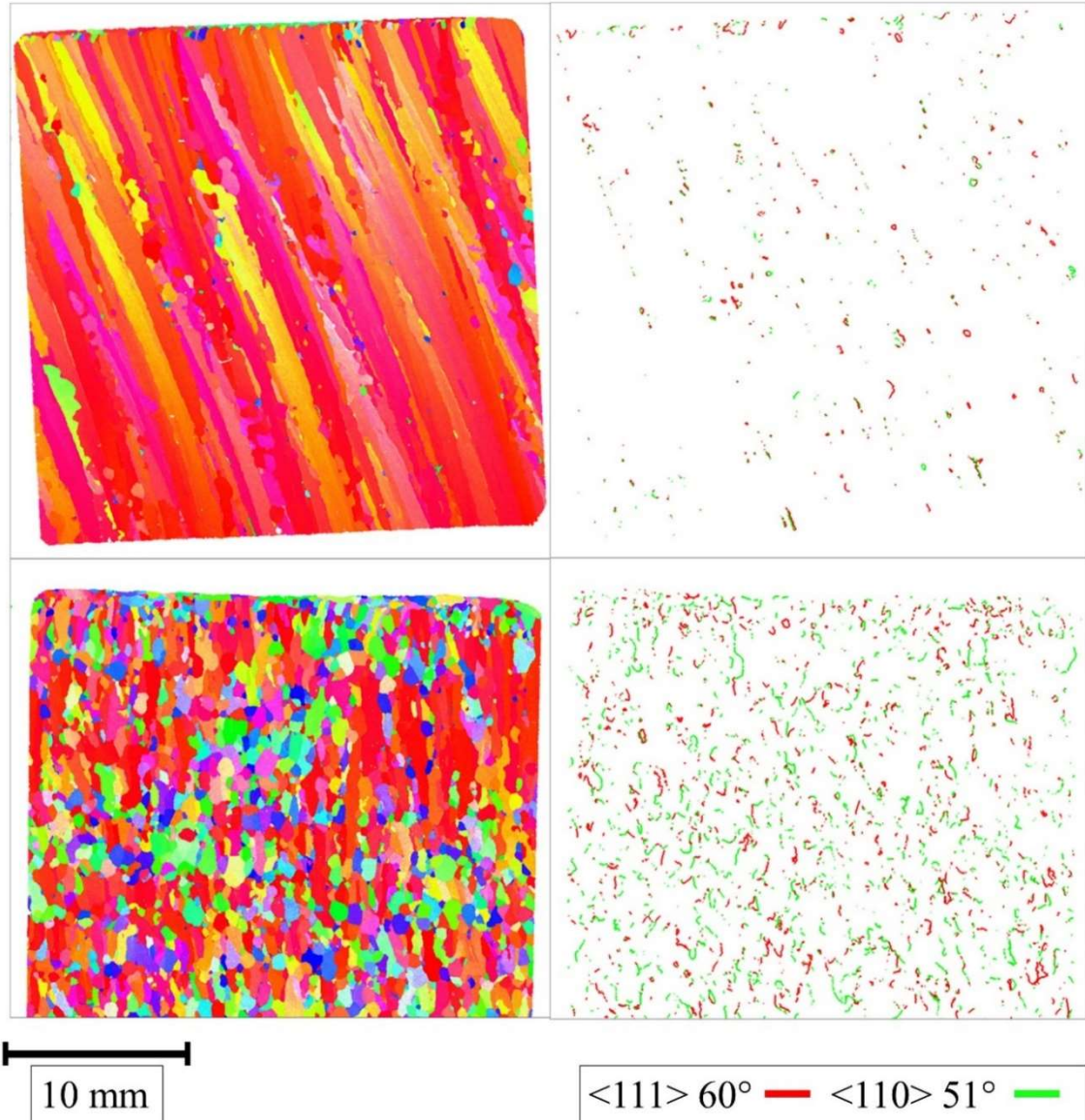


Figure 4-28: Prior- β reconstruction // BD and the $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ grain boundary visualisations from Ti-6Al-2Sn-4Zr-2Mo specimens 3.1 ($36.27 \text{ J} \cdot \text{mm}^{-3}$) and 3.4 ($22.33 \text{ J} \cdot \text{mm}^{-3}$). Note the small, refined grains in specimen 3.1 each appear to contain a minimum of 1 twinned boundary.

Further analysis of the EBSD prior- β reconstructions with IPF colouring with respect to the build direction by Wainwright et al. [4] in the base study for Ti-6Al-4V are presented in Figure 4-29, which exhibited an identical pattern of behaviour with regards to prior- β grain boundary misorientation. For high values of SED and L/D ratio, $\text{LAGB} < 10^\circ$ dominated the specimen. As the SED and L/D ratio was decreased and refinement reaches

an optimum, the misorientations were dominated by the $51^\circ <110>_\beta$ and $60^\circ <111>_\beta$ misorientations. Similarly, there was an increase in the trend to nucleate ahead of the solidification front as a consequence of the reduction in thermal gradient [18], highlighted by the tendency towards the Mackenzie distribution [67], but dominated by primarily 60° misorientation and thus twinning [69,70].

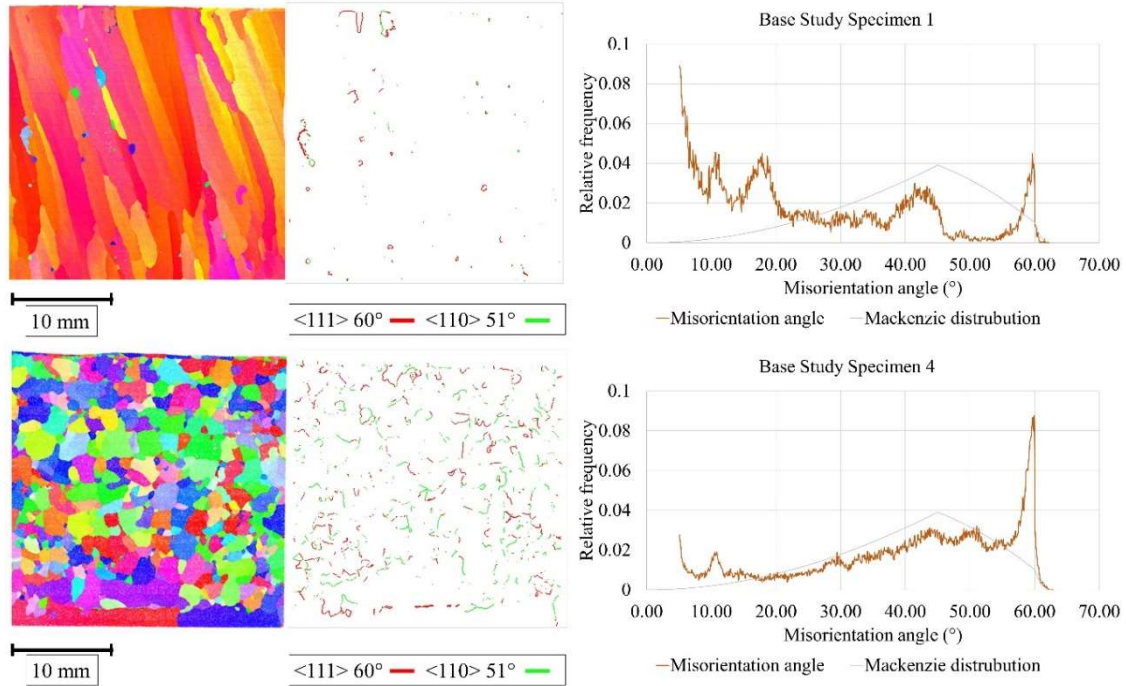


Figure 4-29: Prior- β grain reconstruction // BD, grain boundary misorientation plot and the $51^\circ <110>_\beta$ and $60^\circ <111>_\beta$ grain boundary visualisation from the base study specimens 1 and 4 where optimal grain refinement had been achieved in Ti-6Al-4V ($37.93 \text{ J} \cdot \text{mm}^{-3}$ and $22.28 \text{ J} \cdot \text{mm}^{-3}$). Note the similar misorientation evolution as the Ti-6Al-2Sn-4Zr-2Mo.

For twinned grains to survive and not be outgrown by preferentially orientated $<100>_\beta$ // BD at the bottom of the melt pool surface requires a growth advantage [18]. This came as the rear of the melt pool curvature increased as L/D was reduced and changed the direction of the maximum thermal gradient away from the build direction and encouraged stacking faults at the solidification front. Whilst this mechanism of dendrite twinning has not been previously seen in titanium alloys, it has been recorded in aluminium alloys [71]. However, if this curvature becomes too great the growth advantage becomes too large and seemingly the twinned grains at the rear of the melt pool gain too significant an advantage, leading to the horizontally dominant prior- β grains observed in specimen 1.5 and tilting of grains in the base study at the lowest SED. The IPF // BD prior- β grain reconstruction and misorientation maps are presented in Figure 4-30, confirming the presence of the $51^\circ <110>_\beta$ and $60^\circ <111>_\beta$ misorientations in both specimens. Note for

specimen 1.5 that each horizontal grain starts from a vertical twin boundary. This explains why an optimal L/D ratio of ~ 4 was identified and grain structure became more undesirable as the L/D was reduced beyond this. Further investigation is required in to the effect of twinning behaviour as SED and L/D is reduced to understand its effects, with particular emphasis on solidification modelling to characterise the conditions at the solidification front.

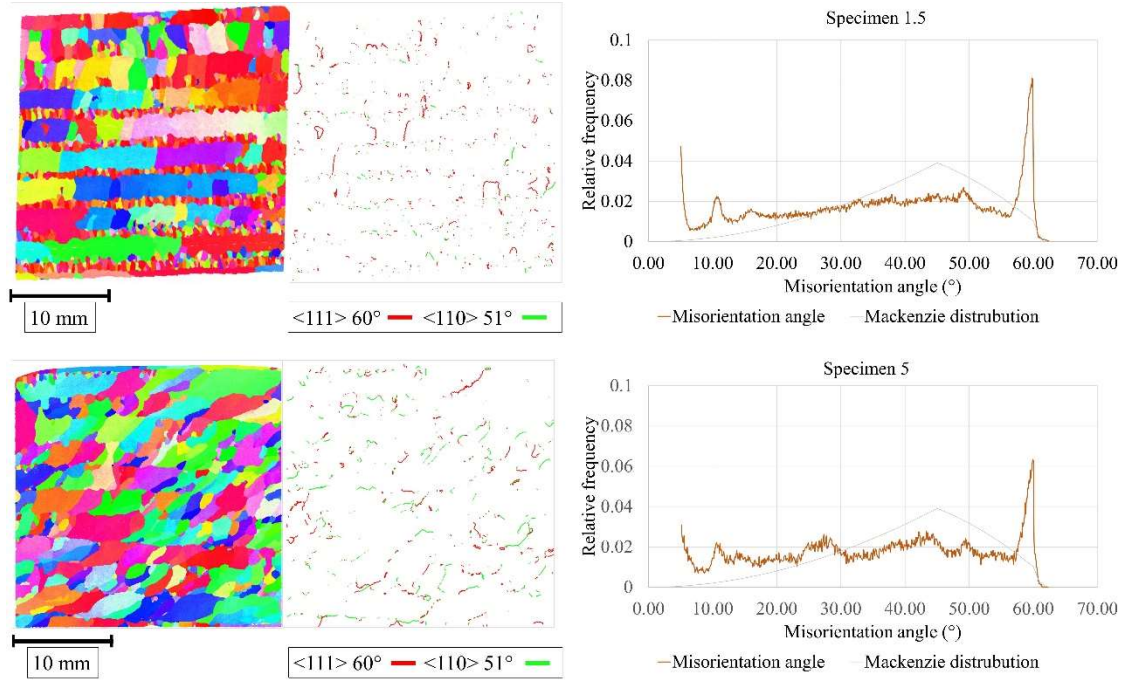


Figure 4-30: Prior- β grain reconstruction // BD, grain boundary misorientation plot and the 51° $\langle 110 \rangle_\beta$ and 60° $\langle 111 \rangle_\beta$ grain boundary visualisation from the Ti-6Al-4V specimen 1.5 and the base study specimen [4], where horizontal grain growth had also occurred in Ti-6Al-4V ($19.96 \text{ J} \cdot \text{mm}^{-3}$ and $21.64 \text{ J} \cdot \text{mm}^{-3}$ respectively).

4.4 Conclusions

The outcomes of this study have demonstrated the effect of reduction in specific energy density of deposited material (SED) on the prior- β grain structure and melt pool shape. With comparison to previous work [4], prior- β grain refinement has been achieved in the as-deposited condition whilst maintaining SED for various deposition parameters and multiple titanium alloy systems. The effect of SED on the mechanical properties was captured via an increase in variation of the microhardness measurements as SED reduced owing to more complex thermal histories and variation of the α microstructure morphologies [57,72]. It was demonstrated that while nucleation ahead of the solidification front appears to influence the refinement of prior- β grains as SED reduced, the primary source was dendrite twinning [69,70] that occurred during solidification. This

was due to an increase in melt pool curvature as SED reduced as observed during EBSD analysis of grain boundary misorientations, determining that melt pool shape is a dominant factor in prior- β grain refinement prediction.

The outcomes of this study can be summarised as follows:

- 1) SED is not primarily responsible for the prior- β grain refinement of titanium alloy systems. Whilst there appears some increase in nucleation ahead of the solidification front through grain boundary misorientations inclination towards the Mackenzie distribution [67,68], the primary form of prior- β grain refinement has been demonstrated to be dendrite twinning that occurs during solidification.
- 2) As the SED is reduced, a reduction in the length/depth ratio of the melt pool geometry is observed, increasing curvature at the rear of the melt pool. This increases the propensity for stacking faults during solidification that lead to a large fraction of $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ misorientations akin to known body centre cubic twinning systems $\{332\}_\beta \langle 113 \rangle_\beta$ and $\{112\}_\beta \langle 111 \rangle_\beta$ respectively [69,70], causing dendrites to twin during solidification.
- 3) If a large enough growth advantage is given to twinned grains via the increase in solidification front curvature, this allows large horizontally orientated grain growth across the width of deposited layers, blocking epitaxial growth.
- 4) The Ti-6Al-2Sn-4Zr-2Mo specimens demonstrated a finer all-round prior- β grain structure as a result of the additional growth restricting elements as compared to Ti-6Al-4V [19,61]. This can be noted by a significantly larger amount of prior- β grains being identified during EBSD analysis.
- 5) The reduction in SED leads to a greater variation in microhardness across all titanium alloy systems deposited as a consequence of changes in cooling rate and α morphology [4,57,72] as SED and thus thermal gradient is reduced.

In conclusion, the impact of this study is significant for the application of process control to refine prior- β control without the need for expensive and potentially limiting post-processing techniques, such as rolling and peening [5,32], melt pool agitation [73] or inoculation [29]. Additionally, a previously unseen refinement mechanism in titanium alloys has been demonstrated in the form of dendrite twinning, something typically seen in other alloy systems such as aluminium [71], rather than by nucleation ahead of the

solidification front. This impact of this study will ultimately provide more design flexibility when considering localisation of grain structure during Wire + Arc Additive Manufacturing built components, with the ability to localise grain structure through process control during deposition. This mechanism of refinement is not without limitation as it is reliant on a small process window that generates unfavourable bead geometries with tall and narrow beads required to generate the high melt pool curvature. Further work is required to optimise this grain structure and improve melt pool shape.

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5. Applicability of Multi-Energy Source Bead Shape Control of Ti-6Al-4V during a Scanning Laser-Arc Wire-Direct Energy Deposition Process

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Abstract

This study demonstrates the laser-arc multi-energy source deposition of Ti-6Al-4V, with independent control of bead geometry from the thermal input. A plasma transferred arc melt pool is used to melt wire feedstock before manipulation of the melt pool shape utilising a fibre laser and galvoscaner. This allows elongation of the melt pool to a desired scan width. Using previously identified processing parameters for mild steel deposition, the applicability to Ti-6Al-4V was first investigated. Once successful bead geometry control was achieved, process parameters more conducive to additive manufacturing were investigated. This included investigation of the specific point energy required to achieve accurate deposition of Ti-6Al-4V and minimal penetration. With successful and accurate control of the melt pool shape achieved, control of the melt pool shape to influence the prior- β grain structure of Ti-6Al-4V was investigated. Having previously been identified as a primary factor in prior- β grain morphology, a scan strategy was implemented such that an oscillated path with fixed scan width and various amplitudes was investigated to elongate the melt pool length. Scan frequency remained constant to ensure the same specific point energy. The results demonstrated that a mixed prior- β grain morphology could be transformed to a columnar morphology, whilst the specific energy density of deposited material and heat input remained constant, whilst only the melt pool shape was altered. Geometry and microstructure analysis was conducted using multiple techniques including optical microscopy and electron backscattered diffraction. Microhardness results of the wall specimens demonstrated minimal change across the differing scan amplitudes, inferring minimal differences in cooling rate and α lath sizing.

5.1 Introduction

Direct energy deposition (DED) additive manufacturing (AM) processes have come under intense academic and commercial scrutiny given their undeniable benefits when compared with traditional manufacturing techniques such as casting, subtractive manufacturing and forgings [1]. These benefits include a reduction in cumulative energy demand, cost reduction and design freedom in terms of complex geometry and microstructural properties [2–4]. During metal additive manufacturing (MAM), metallic components are created through the successive melting or sintering of tracks layer-by-layer using a laser, arc or electron beam energy source and wire or powder feedstock [2]. The deposition of large-scale components such as those associated with the aerospace sector, are well suited to the Wire + Arc Additive Manufacturing process (WAAM). This process provides substantially high deposition rates, depositing in kilograms per hour and does not suffer from process induced porosity [4,5]. A multi-energy source (MES) wire-DED process is one that deposits components with a wire feedstock and multiple thermal energy sources, typically a combination of arc and laser energy sources. The purpose of combining energy sources is to mitigate limitations and combine advantages of the respective energy sources [6].

Conventional arc energy sources used for WAAM include plasma transferred arc (PTA) [7], metal inert gas (MIG) [8] and tungsten inert gas (TIG) [9]. Specific configurations such as cold metal transfer (CMT) [10], pulsed-TIG [11] and pulsed-PTA [12] exist. All arc processes face the same limitations with respect to bead geometry control, which is a reliance on changes to heat input. An inversely proportional relationship exists between arc energy and bead geometry, such that neither can be independently manipulated [13]. Additionally, this ensures that the microstructure generated is invariably linked to the bead geometry as a consequence of the heat input [14,15]. It is typical of WAAM processes to generate preforms rather than near net-shape components as a consequence of the high deposition rate achieved [16].

Conventional laser welding processes incorporate the use of CO₂, neodymium-ytterbium-aluminium-garnet (Nd:YAG), fibre and diode lasers. Each type of laser operates at a specific wavelength, dictating the energy absorptivity for different materials [17]. In comparison to arc energy sources, laser energy sources generate small melt pools, as a

consequence of concentrated energy in small beam diameters, and generate high penetration. During laser AM, it is not uncommon for the laser to be defocussed to increase melt pool diameter, this transitions the keyhole operation to conduction mode, giving comparatively larger and shallower melt pools conducive to AM [18]. However, the melt pool remains smaller than arc processes and laser processes exhibit higher cooling rates than WAAM, but benefit from higher shape fidelity [16]. In comparison to arc processes, laser process have the ability, through beam profiling [13], to alter the distribution of energy across the beam area giving greater control of bead geometry for a fixed energy input. The combination of arc and laser energy sources provides the opportunity for the high deposition rate achievable in WAAM, whilst benefitting from melt pool shape control and improved part fidelity from laser AM [6]. A large proportion of MES laser-arc processes use a stationary or oscillating laser leading the arc, operating in a keyhole mode to improve shape fidelity.

Ma et al. [19] investigated the use of an oscillating laser leading a pulsed CMT arc process to deposit Al-6Mg-0.3Sc. The laser was oscillated at 200 Hz across a 2 mm width, in a circular pattern operating in keyhole mode through a 0.4 mm beam diameter. The results demonstrated that the surface roughness decreased by 34% and effective wall width increased by 20%. This can be attributed to the increase in melt pool area as a consequence of the increased heat input from the combined energy sources, reducing the overall surface curvature and increased depth of penetration. The oscillation provided a stirring effect within the melt pool interrupting the fluid flow, which provided an environment for epitaxial dendritic growth to be disrupted by dendrite fragmentation. Analysis of the grain boundary misorientations demonstrated that the grain boundaries followed the Mackenzie distribution [20] for polycrystals. Therefore, a fully equiaxed grain structure that removed anisotropic tensile properties was deposited. An additional benefit from the generation of the keyhole combined with stirring, was to allow gases that would be usually trapped to escape the melt pool, reducing porosity by 71% compared with single energy source CMT deposition of the same alloy.

A similar response was reported by Gong et al. [21] when conducting an equivalent oscillated laser-arc process for the deposition of 316 stainless steel. In this study Gong et al. [21] also considered the use of a stationary laser leading the arc for comparison to the oscillated laser-arc and WAAM processes. When the laser was stationary no reduction in

porosity, when compared to the single energy source CMT deposition was observed. Nor was there a refinement of the columnar grain structure compared with the oscillated sample confirming the effect of oscillation on the melt pool flow dynamics to refine grain structure and prevent porosity. Tensile anisotropy was eliminated for the oscillated laser-arc process, whilst significant vertical and horizontal differences were recorded for the WAAM and stationary laser process, as a consequence of the columnar grains. However, whilst beneficial to the grain structure and porosity, this method reduces process efficiency, by generating a large area of remelting [6].

Conversely, researchers such as Kapil et al. [22] have found benefits in utilising a stationary laser-arc MES system, where the laser leads the melt pool. During the deposition of HT780 MAG wire, the addition of the stationary laser increased the size of the melt pool and prevented spatter from being generated during a back-fed CMT process. Their results demonstrated that the bead height was maintained regardless of process parameter variation, recording only a difference in the bead width and penetration depth. However, the results are somewhat misleading. A significant level of undercut can be observed which was taken into account as part of the bead geometry measurements, demonstrating that the process is far from being optimised and that the melt pool flow was insufficient. For a fixed deposition rate, with adequate melt pool flow, the increase in bead width would lead to a reduction in bead height. This has been demonstrated by Wang et al. [23], who investigated the applicability of a plasma arc-laser hybrid for the deposition of Ti-6Al-4V.

Wang et al. [23] studied the effect of various laser and arc process parameters on the bead geometry during a MES laser-arc hybrid process, where the laser was leading the PTA melt pool. In this study when the total heat input as a result of arc or laser energy increased, the bead height decreased as bead width increased, as expected, unlike the findings of Kapil et al. [22]. Wang et al. [23] also demonstrated that the beam diameter had little effect on the bead shape despite being increased by a factor of 3, as the total energy input remained constant. Pardal et al. [24] noted a similar effect when studying the laser stabilisation of a CMT arc process utilising a laser concentric with the arc centre. They determined that the surface roughness was stabilised and that total energy input of the laser was responsible for the bead width and not beam diameter. However, neither considered that as the beam diameter increased, with a constant laser power, there would

be a corresponding reduction in power density, which would likely result in different localised cooling rates and microstructures despite having the same total heat input. Ultimately, the results of the study by Wang et al. [23] identified that the optimum configuration for the laser-arc MES process is when the PTA is used to melt the wire feedstock and the melt pool size is controlled via the laser. This is a consequence of the higher melting efficiency during WAAM compared to laser AM [6].

Wang et al. [25] further investigated the deposition of Ti-6Al-4V with a dual laser-arc MES process having identified an optimal configuration, with the PTA used to melt the wire feedstock and laser to control melt pool shape. Dual stationary lasers positioned to the side and rear of the melt pool were used to elongate the total melt pool area. In comparison to the previous MES processes mentioned, Wang et al. [25] operated in conduction mode. This is more conducive to additive manufacturing by improving process efficiency and reducing remelting [6]. Their results demonstrated that independent control of the bead geometry and deposition rate could be achieved in the deposition of Ti-6Al-4V. However, it was imperative that a quasi-steady state melt pool was generated. When independent melt pools from the multiple energy sources were formed, the feedstock material from the PTA melt pool was unable to successfully flow, generating poor surface quality and defects. Wang et al. [25] successfully deposited several walls up to 18.6 mm wide, whilst maintaining negligible surface roughness. Whilst this work did not explicitly consider the microstructure generated, it was evident that a columnar prior- β grain structure existed.

Hao et al. [26] also demonstrated the importance of maintaining a quasi-state melt pool to form large melt pool widths. They investigated the use of an oscillating laser on weld bead shape. Their results demonstrated that deposition of a sawtooth pattern is generated if the oscillating frequency is not large enough to incur sufficient overlapping. Whilst not discussed, it can be deduced that the increase in oscillating frequency would ensure that the melt pool had not solidified before the return path of the laser ensuring a continuously wide quasi-steady state melt pool as highlighted by Chen et al [13].

Previous literature has focused on the improvement of process stability and bead surface quality rather than the ability to control the melt pool shape during deposition. Melt pool shape has been identified by Wainwright et al. [27] as being a controlling factor in the

prior- β grain morphology of Ti-6Al-4V in the as-deposited condition. Chen et al. [13] presented a novel process to enable independent control of bead width and bead height that may be applicable to controlling refinement. Through the application of a scanning laser and arc MES process to deposit mild steel, the PTA energy source was used to form an initial melt pool and melt the wire feedstock. Additionally, a laser and galvoscaner were used to extend the melt pool behind the arc to a specified width, ensuring a quasi-steady state melt pool was generated. With this arrangement Chen et al. [13] were able to demonstrate that independent control of bead width and bead height could be obtained, with dynamic width control during deposition. It was demonstrated that the bead width and travel speed were controlled by the scanning width, whilst the bead height was controlled by the wire feed speed (WFS). However, the study only considered the generation of a quasi-steady state melt pool in a single direction, perpendicular to the deposition direction. To consider the effects of melt pool shape on prior- β grain refinement of Ti-6Al-4V as suggested by Wainwright et al. [27], both the melt pool shape perpendicular and parallel with deposition direction need to be controlled to alter the melt pool curvature [27].

The purpose of this paper was to determine the applicability of the novel scanning laser and arc MES process proposed by Chen et al. [13] to the deposition of Ti-6Al-4V, noting variation in the thermal fluid properties of steel and titanium [28]. This enabled independent control of the melt pool shape and provided a mechanism to study the effect of melt pool shape on the prior- β grain structure of Ti-6Al-4V. Previous work by Wainwright et al. [27] demonstrated the effect of melt pool shape on prior- β grain structure, but was unable to isolate the specific energy density (SED) variable from bead geometry. Utilising the process proposed by Chen et al. [13], the SED can be maintained and the melt pool geometry isolated and thus its effect characterised independently.

5.2 Theory

5.2.1 Specific Point Energy

During the MES process the addition of the laser energy source allows for configuration of the specific point energy which can be used to alter the melt pool shape [13,23,24]. When the laser irradiates the surface, the energy delivered to a singular point is referred

to as the specific point energy [29]. The specific point energy (J) is determined by the product of power density ($\text{W} \cdot \text{mm}^{-2}$), interaction time (s) and interaction spot area (mm^2) as described in Equation 5-1 [29].

$$E_{sp} = q_p \cdot \tau_i \cdot A_s = P \cdot \tau_i \dots \dots (5-1)$$

Where E_{sp} represent specific point energy, q_p represent power density, τ_i represents interaction time, A_s represents beam area and P represents the laser power.

As determined by Chen et al. [13], during the scanning laser process, a sawtooth pattern is formed as the melt pool advances as demonstrated in Figure 5-1. This means that a specific point is irradiated numerous times by the laser during deposition and is determined by the beam diameter and scan frequency. For the MES process used in this study, the specific point energy is determined by Equation 5-2 [13], where n_i represents the number of interactions.

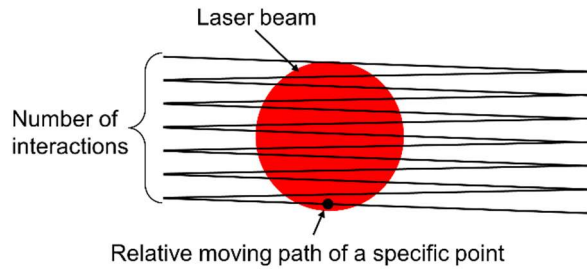


Figure 5-1: Sawtooth pattern generated by scanning laser during deposition.
Reproduced from [13].

$$E_{sp} = \sum_1^{n_i} q_p \cdot \tau_i \cdot A_s = \sum_1^{n_i} P \cdot \tau_i \dots \dots (5-2)$$

To calculate the number of interactions of a specific point, two calculations initially need to be made, the scanning frequency (Equation 5-3) and the amplitude of the sawtooth pattern (Equation 5-4). Subsequently, the number of interactions can be calculated by Equation 5-5 [13].

$$F_s = \frac{v_s}{2w_s} \dots \dots (5-3)$$

Where F_s represents scanning frequency, v_s represents the scanning velocity and w_s represents the scanning width.

$$A_o = \frac{v_a}{F_s} \dots \dots (5-4)$$

Where A_o represents the amplitude of the oscillation pattern and v_a represents the travel speed during deposition.

$$n_i = \frac{B_d}{A_o} \dots \dots (5-5)$$

Where B_d represents the beam diameter.

5.2.2 Specific Energy of Deposited Material

The specific energy density of deposited material differs from the specific point energy of the laser. Instead of considering the total energy delivered to a single point, it considers the total combined energy of the arc and laser per unit volume of deposited material. This is derived in Equation 5-6 as adapted from Wainwright et al. [30] to incorporate the addition of the laser energy source with an absorptivity coefficient of 0.45, based upon existing literature [31,32].

$$SED (J.mm^{-3}) = \frac{4(\eta_A VI + \eta_L P)}{WFS * \pi d^2} \dots \dots (5-6)$$

Where η_A represents arc efficiency, V represents arc voltage, I represents arc current, η_L represents laser absorptivity coefficient, P represents laser power, WFS represents wire feed speed and d represents wire diameter.

5.2.3 Bead Geometry Prediction

With independent control of the bead geometry from the energy input, the relationship can be explained geometrically based upon the rate of deposition to provide a bead geometry prediction. Consider Equation 5-7, which is a standard expression of the deposition rate [33], i.e. the amount of wire fed per second.

$$R = \frac{\pi d^2}{4} \cdot WFS \cdot \rho \dots \dots (5-7)$$

Where WFS represents wire feed speed and ρ represents the wire density. Correspondingly, the deposition rate may also be considered as an expression of the cross-sectional area of the deposit as seen in Equation 5-8. Chen et al. [13] considered this as a

rectangle, however, the Ti-6Al-4V MES deposited beads were more ovular in nature and so an ovular relationship was considered.

$$R = \pi \cdot \frac{W}{2} \cdot H \cdot v_a \cdot \rho \dots \dots (5-8)$$

Where W represents bead width, H represents bead height and v_a continues to represent travel speed. Deposition rate can now be expressed in terms of the volume of wire fed per second and the deposited geometry as expressed in Equation 5-9.

$$\frac{\pi d^2}{4} \cdot WFS \cdot \rho = \pi \cdot \frac{W}{2} \cdot H \cdot v_a \cdot \rho \dots \dots (5-9)$$

Equation 5-9 can be used to determine the processing parameters required to deposit a specific bead geometry. For example, in Equation 5-10, it can be determined that when the scanning width is controlled by the scanning laser and if the specific point energy is maintained through an equivalent Wv_a , the bead height (H) is determined by the WFS.

$$H = \frac{d^2}{2} \cdot \frac{WFS}{Wv_a} \dots \dots (5-10)$$

5.3 Methodology

Several processing parameter conditions were considered during the investigation of this study and will be discussed in their respective sections. In summary, a preliminary investigation with equivalent processing parameters to Chen et al. [13] was conducted to test the applicability of the novel MES system to the deposition of Ti-6Al-4V. Noting the low travel speed of deposition used in Chen et al. [13], subsequent investigation into increasing the travel speed of deposition to a regime more conducive to additive manufacturing was conducted. In addition to the SED, which considers the total energy input per volume of deposited wire, with the additional laser energy source of the MES system an investigation into the required specific point energy to deposit Ti-6Al-4V was conducted to improve melt pool shape accuracy (which among other parameters is dependent on the number interactions of the scanning laser over a single point). Finally, an investigation into applicability of melt pool shape control to alter prior- β grain morphology of Ti-6Al-4V, continuing the work presented by Wainwright et al. [27]. This required the deposition of several walls with fixed SED and various melt pool shapes.

The experimental setup may be observed in Figure 5-2, whereby samples were deposited on to Ti-6Al-4V substrate clamped to an aluminium backing plate. Various substrate sizes were utilised dependent on the scan width and will be detailed in their relevant sections. Deposits were conducted with a single pass, single direction strategy using an Aerotech A3200 controller and 3 axis CNC Aerotech stage gantry system. A PWP Viper MC plasma torch at 15° offset and EWM 352 DC power source were used to create the initial melt pool, trailed by an unpolarised SPI 6KW continuous wave fibre laser (1.08 μm wavelength) with gaussian beam profile. Various scan widths were considered and manipulated via an IPG highspeed galvoscanner controlled by IPGWeld software. A laser-arc offset of 10 mm was used, having been identified as the optimal configuration from Chen et al. [13] where the laser scan width clips the PTA melt pool. A defocused 4 mm beam diameter was generated, to ensure that the melt pool operation mode was by conduction. Dual Migatron KT4 wire feeders were used to front feed wire to the centre of the arc at an inclination angle of 5° and offset of 10°. All samples were deposited inside a globally shielded environment purged with UN1006 Pureshield Argon and maintained at an oxygen level of < 500 PPM, monitored with a Argweld PurgEye 600. The composition of the wire feedstock used in this study is detailed from the manufacturer and available in Table 5-1.

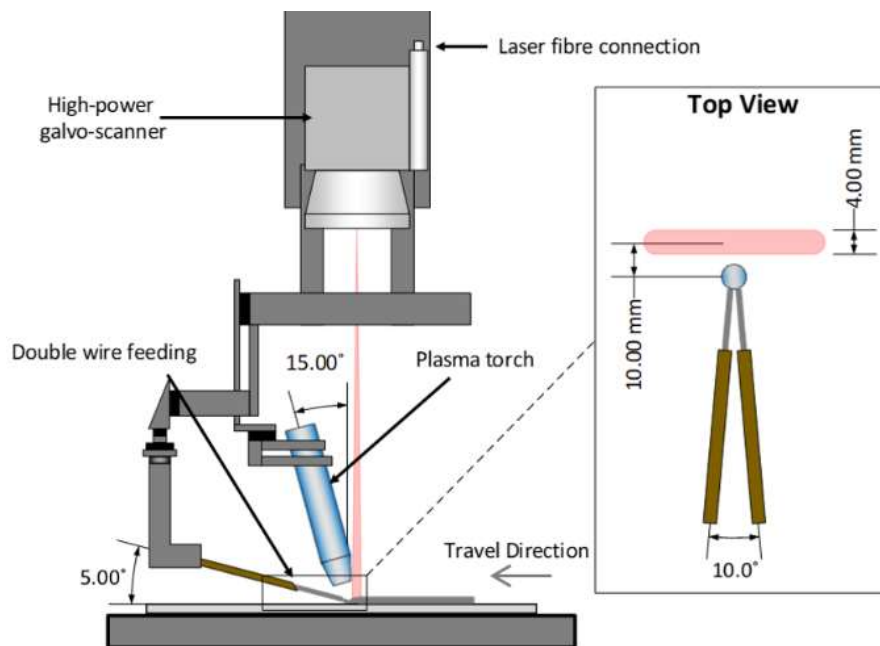


Figure 5-2: Experimental setup schematic for MES source system combining PTA and fibre laser with galvoscanner.

Table 5-1: Wire feedstock composition Ti-6Al-4V (wt %)

O	N	C	Fe	Al	V	Si	H	Ti
0.15	0.008	0.021	0.18	6.14	3.94	0.012	0.0004	BAL

During deposition all samples were monitored via a Xiris XVC-1100 processing camera mounted perpendicular to the melt pool and monitored to ensure process stability and consistent droplet feedstock transfer mode. To ensure high image quality, the camera aperture was set to the manufacturer's minimum and a rolling shutter mode with 10 μ s exposure time. A Xiris 50 mm lens with UV filter and spatter protection was used. During deposition of multi-layer specimens, all layers were allowed to cool to $< 40^{\circ}\text{C}$ before deposition of the successive layer. This was to ensure that no variability in pre-deposition temperature occurred. A pre-defined cooling time would not account for this, due to changes in the thermal mass as layers are deposited.

Post deposition, cross-section and longitudinal samples were extracted for geometry and microstructural analysis from the central section of each specimen. Samples were mounted in conductive phenolic resin via a hot mounting press. All samples were mechanically polished using consecutively higher grades of silicon carbide paper from 240 to 2000 grit, before a final polish using colloidal silica and oxalic acid and etching with Kroll's reagent for ~ 10 seconds to reveal the $\alpha + \beta$ microstructure. Optical microscopy was conducted using a Hirox RH-2000 for large area mapping at a magnification of 50x. Geometrical measurements of the melt pool were conducted using AxioVision 4.8. In all cases, bead geometry was measured using the definitions described by Brandl et al. [34] as detailed in Figure 5-3. Given the propensity for epitaxial columnar growth in Ti-6Al-4V during WAAM [2,35,36], the melt pool penetration depth was taken from the beginning of columnar prior- β grain growth.

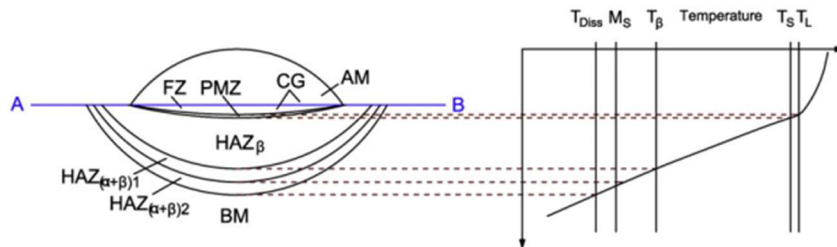


Figure 5-3: Correlation of temperature and resulting microstructural zone, used for geometrical measurements of the bead geometry (FZ – Fusion zone, PMZ (Partially melted zone, CG -Columnar growth, AM – Added material, HAZ – heat affected zone, BM – Base metal, T_{Diss} – α dissolution temperature, M_S – Martensite starting temperature, T_S – Solidus temperature, T_L – Liquidus temperature). Reproduced from [34].

Electron backscattered diffraction (EBSD) analysis was conducted on the wall specimens using a Thermo Scientific Apreo C FEG-SEM at 20 kv accelerating voltage and 51 nA beam current at a step size of 15 μm and processed using Oxford Instruments AztecCrystal software. The allotropic nature of Ti-6Al-4V means that it performs a solid-state transformation from $\beta \rightarrow \alpha + \beta$ during cooling, therefore the β phase cannot be observed directly at room temperature. However, the transformation follows Burger's orientation relationship (BOR), i.e. $\{110\}_{\beta} // \{0001\}_{\alpha}$ and $\langle 111 \rangle_{\beta} // \langle 0001 \rangle_{\alpha}$ [37], which allows prior- β grain reconstruction based off explicit orientation relationships between α variants and parent grain β . The acquired room temperature $\alpha + \beta$ phase data was subject to parent grain reconstruction developed by Davies and Wynne [38,39], with up to 3° divergence from BOR considered to be part of the same grain and up to a 2° misorientation from a particular variant accepted to allow for reconstruction errors. Quantitative analysis of the prior- β reconstructions was conducted using Oxford Instruments AztecCrystal software.

Microhardness measurements were conducted on the final wall specimens through a Innovatest Falcon 503 hardness machine using the Vickers method. A 300 g load was selected and 10 second load time with 0.5 mm indent separation from the manufacturers recommendation. A total of 37 measurements were taken along the central line of each specimen, from the top to bottom of the sample post-polishing and EBSD analysis.

5.4 Results and Discussion

5.4.1 Applicability of Scanning Laser-Arc MES Deposition of Ti-6Al-4V

A preliminary investigation of the applicability of the MES system proposed by Chen et al. [13] was conducted with Ti-6Al-4V wire feedstock and substrate (100 mm x 175 mm x 10 mm) to deposit 80 mm long single bead on plate tracks. Chen et al. [13] successfully demonstrated the independent control of the bead width and bead height with mild steel deposition and as such two parameter sets were selected for replication in Ti-6Al-4V. The purpose of this preliminary investigation was to identify processing nuances that may occur when utilising a different equipment setup and alloy with differing thermal characteristics [28].

Four samples were deposited per study with a WFS of 5.0, 13.1, 18.5 and 23.8 mm.s⁻¹ as replicated from Chen et al. [13] therefore, eight samples in total. The process parameters used during this preliminary investigation are detailed in Table 5-2.

Table 5-2: Process parameters utilised during preliminary investigation of MES applicability to Ti-6Al-4V

ID	Laser Power (W)	Arc Current (A)	Scan Speed (mm.s ⁻¹)	Scan width (mm)	Travel Speed (mm.s ⁻¹)
PI 1	3000	140	500_16500_500	6.5_3.5_6.5 (16.5)*	0.8
PI 2	3000	140	500_16500_500	8.25_3.5_8.25 (20.0)*	0.67

*Note the combine scan width in PI 1 = 16.5mm and PI 2 = 20mm

With consideration of Equation 5-2, it becomes clear that as the scanning width was increased from 16.5 mm to 20 mm, to maintain an equivalent specific point energy requires the reduction of the travel speed. If the same travel speed were maintained for the 20 mm scan width as the 16.5 mm, a lower number of interactions would occur. As interaction time remains constant due to the beam diameter and scanning velocity remaining consistent, a lower specific point energy would be delivered. To ensure an equivalent specific point energy required a reduction in travel speed as scanning width increased to maintain an equivalent number of point interactions [13]. This ensured that the melt pool geometry was being controlled independently by scanning technique rather than the thermal energy input. The specific point energy of the samples in PI 1 was calculated as 1818.18 J and PI 2 as 1791.04 J using scanning widths of 16.5 mm and 20 mm respectively.

As discussed by Chen et al. [13], to prevent excessive laser energy in the centre of the scan width where arc energy is also delivered, the scan pattern was divided into 3 lines. Where the arc energy was delivered, the scanning speed was increased to the maximum of 16,500 mm.s⁻¹ for a fixed distance of 3.5 mm. The scan speed on either side of the central distance remained constant at 500 mm.s⁻¹. The scan path alternated direction, i.e. left to right and right to left, generating a sawtooth pattern as the melt pool advanced. A schematic is provided in Figure 5-4.

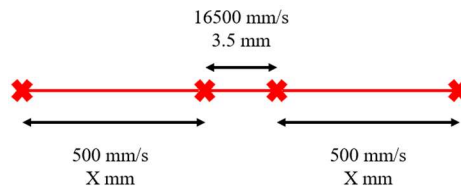


Figure 5-4: Schematic of 3-line scan strategy to avoid unnecessary energy delivery to scan width centre.

The macrographs of PI 1 where a 16.5 mm combined scan width was used may be observed in Figure 5-5, with both the as-deposited samples and cross-section macrographs taken at the centre of the deposits. Inspection of the deposited samples demonstrated a large ovular melt pool shape, as opposed to the rectangular melt pool seen by Chen et al. [13]. However, it was clear that the melt pool width had elongated with the scanning width as intended. Investigation of the macrographs confirmed the presence of a large heat input from the microstructure. There is a clear large heat affected zone (HAZ) present. This led to significant prior- β coarsening, evident across the entire substrate thickness. This may be explained by the significantly large heat input that is obtained from a travel speed of 0.8 mm.s^{-1} [15]. The effect of the large heat input may also be observed by the introduction of porosity in the sample at the sample surface. This demonstrates that during the course of deposition excessive energy led to ablation of the bead surface and vaporisation of the deposited material, which was observed as vapor plumes leaving the surface during deposition [40].

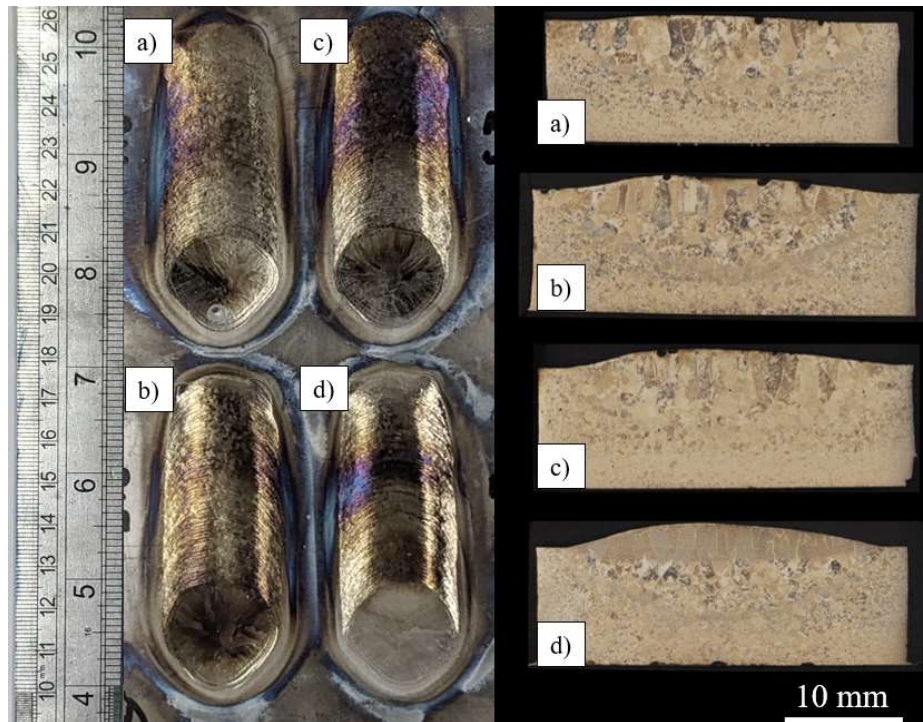


Figure 5-5: (L) As-deposited Ti-6Al-4V specimens of PI 1 using MES system with scan width of 16.5 mm with multiple wire feed speeds of a) 5.0 mm.s^{-1} , b) 13.1 mm.s^{-1} , c) 18.5 mm.s^{-1} , d) 23.8 mm.s^{-1} . (R) Etched cross-sections from deposition centre.

The bead geometry was measured using the definitions outlined by Brandl et al. [34]. As may be observed in Figure 5-6, the increase in WFS led to an increase in the bead height from $\sim 0.50 \text{ mm}$ to $\sim 2.00 \text{ mm}$, whilst the bead width remained constant at $\sim 27.50 \text{ mm}$.

In all cases the measured penetration depth was significant at ~ 5.50 mm and as expected the contact angle increased as WFS and thus bead height increased. As to be expected, given that a scan width larger than the arc melt pool width was specified and that the heat input remained constant across all specimens, the same bead width was measured in all cases. The increase in bead width over the specified scan width was not surprising, given the excessive heat input at low travel speeds. This heat input was also responsible for the low process efficiency expressed by the large penetration depth [6].

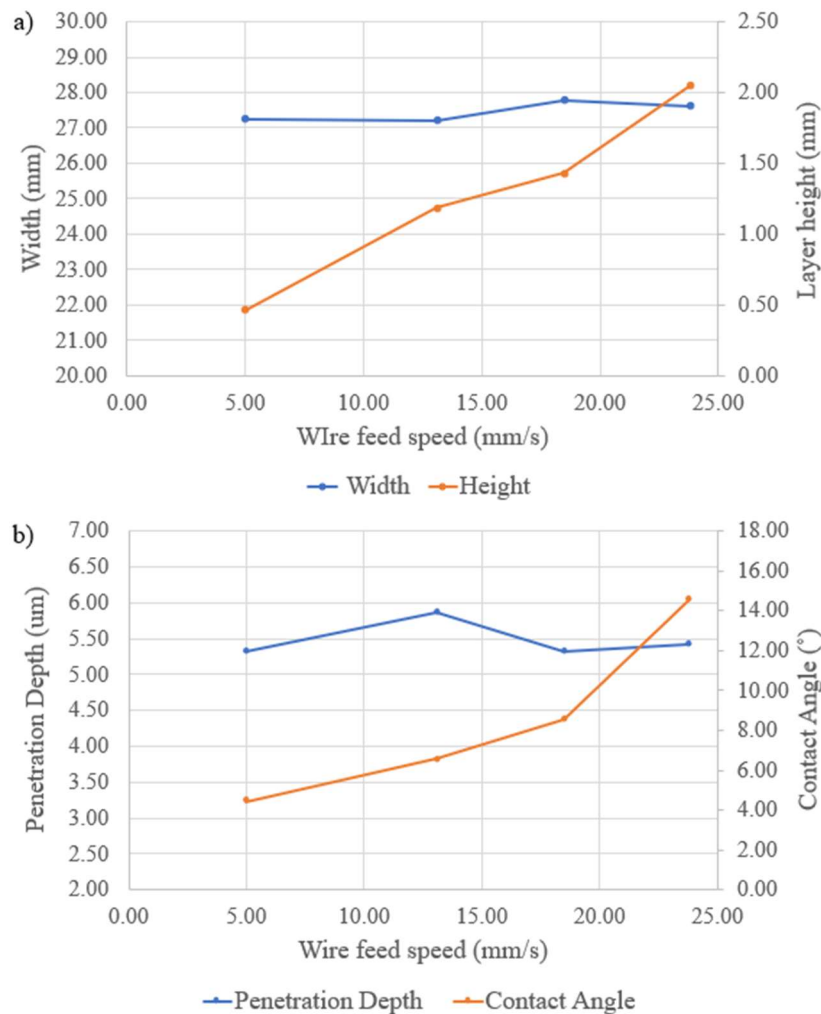


Figure 5-6: Bead geometry measurements from cross-sections of PI 1 specimens a) Bead width and height, b) Penetration depth and bead contact angle with substrate.

Both the as-deposited samples and cross-section macrographs taken at the centre of the deposited sections for PI 2 specimens may be observed in Figure 5-7. A 20 mm combined scan width was used through increasing the scanning distance on the outer edges as compared to PI 1 and travel speed reduced to maintain specific point energy.

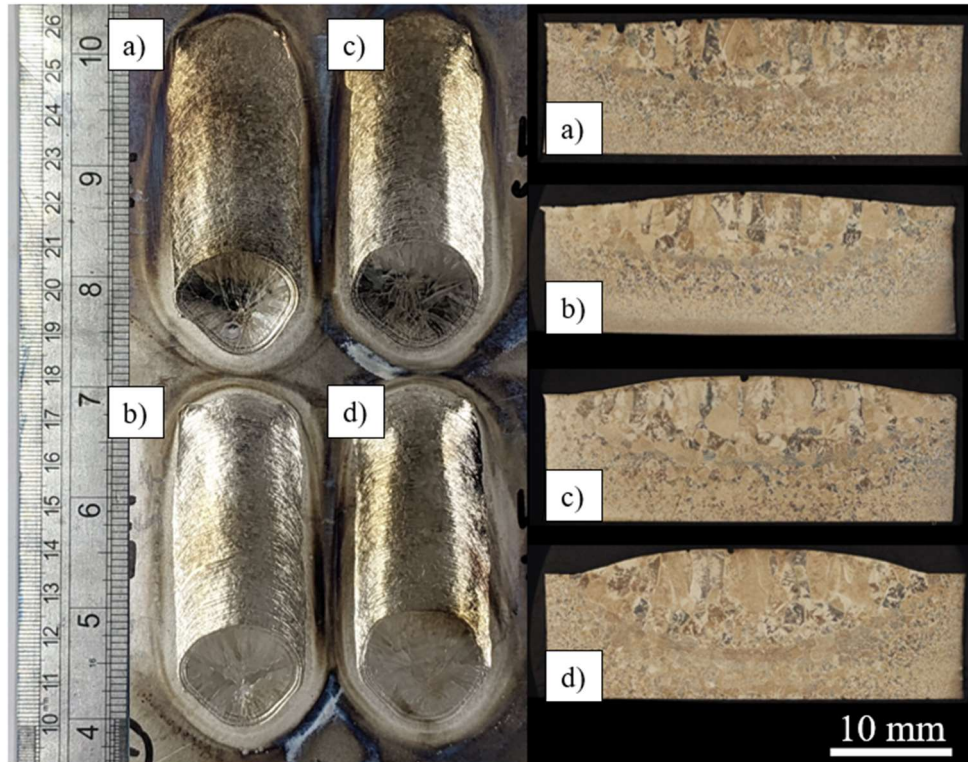


Figure 5-7 (L) As-deposited Ti-6Al-4V specimens of PI 2 using MES system with scan width of 20 mm with multiple wire feed speeds of a) 5.0 mm.s⁻¹, b) 13.1 mm.s⁻¹, c) 18.5 mm.s⁻¹, d) 23.8 mm.s⁻¹. (R) Etched cross-sections from deposition centre.

The PI 2 specimens with increased scan width, similar to PI 1, also demonstrated a large ovular melt pool shape rather than rectangular as seen by Chen et al. [13]. The PI 2 specimens showed an identical geometry and microstructural evolution as PI 1, with an elongated melt pool width and severe prior- β grain coarsening demonstrated by the large primary HAZ across the thickness of the substrate for each specimen. The PI 2 specimens also demonstrated evidence of vaporisation [40] by the formation of tiny pores at the surface of the deposited beads. In the case of PI 1 and PI 2 specimens, the final bead geometry appeared ovular in nature when considering the bead cross-section. The bead geometry of the PI 2 specimens may be observed in Figure 5-8.

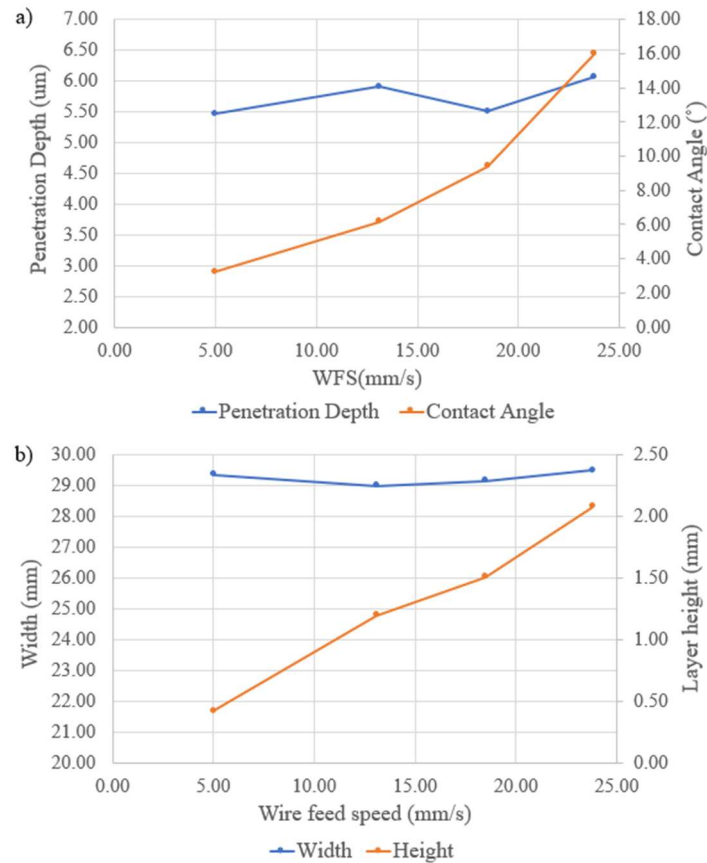


Figure 5-8: Bead geometry measurements from cross-sections of PI 2 specimens a) Bead width and height, b) Penetration depth and bead contact angle with substrate.

The bead geometry from PI 2 show the same trend as the results from PI 1. As WFS increased, an increase in the bead height from ~ 0.50 mm to 2.00 mm was recorded, whilst the bead width remained constant at ~ 29.00 mm. The penetration depth was equivalent at ~ 5.50 mm and the contact angle increased as WFS and thus bead height increased. Given an equivalent specific point energy across both the PI 1 and PI 2 specimens, the same penetration depth was expected, however, the heat input from the arc would be larger in PI 2 as a consequence of the reduced travel speed [41]. No observable change in penetration depth was observed from this, however, the reduction in travel speed from 0.8 mm.s^{-1} to 0.67 mm.s^{-1} was negligible and thus no measurable variation in the penetration depth was expected.

In both PI 1 and PI 2, the total measured melt pool width was greater than the desired scan width indicating an excessive heat input. A similar effect was observed by Chen et al. [13], however the effect was not as severe. This highlights the difference in the thermal properties of the steel and titanium during MES laser-arc welding. Regardless, this effect

corroborated with previous research conducted by Pardal et al. [24], that demonstrated that the heat input from the laser energy source during a MES system can increase the melt pool geometry. Nevertheless, it can be observed from Figure 5-9 that despite an excessive heat input, independent control of bead geometry had been achieved, with bead height being maintained for differing bead widths.

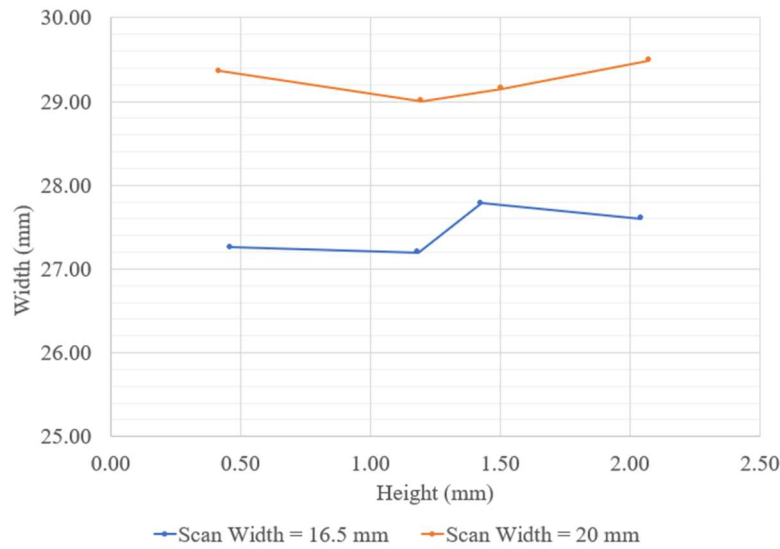


Figure 5-9: Comparison of bead geometry for PI 1 and PI 2. Note that bead width and height can be controlled independently.

Overall results from the PI 1 and PI 2 specimens confirm the applicability of the novel MES process proposed by Chen et al. [13] for the deposition of Ti-6Al-4V. However, an increase in travel speed was required to reduce the heat input, such that the bead width was only controlled by scanning width and excessive remelting was avoided as this decreased process efficiency and is not conducive to the concept of additive manufacturing [1,6].

5.4.2 Increasing Travel Speed during Deposition

In the preliminary investigation, as a consequence of the slow travel speed, excessive heat input caused the bead width to be greater than the desired scan width. The purpose of this subsequent study was to increase the travel speed and WFS to a workable regime with respect to WAAM, that typically deposits upwards of 2 mm.s^{-1} and where bead height is greater than penetration depth [2]. As denoted in Equation 5-2, to maintain an equivalent specific point energy to the preliminary investigation, with travel speed increased and all other parameters remaining constant, a decrease in scan width to 6.75 mm was required,

resulting in a specific point energy of 1777.77 J. Given the shorter scan width, a single path scan strategy was used at 500 mm.s⁻¹ due to limitations of the galvoscanner. Four specimens were deposited with WFS of 24.40 mm.s⁻¹; 37.97 mm.s⁻¹; 45.03 mm.s⁻¹ and 51.87 mm.s⁻¹, to ensure that independent bead height and width was maintained. The substrate used in this study was Ti-6Al-4V (25 mm x 100 mm x 10 mm). 80 mm single track beads were deposited. The process parameters used may be observed in Table 5-3.

Table 5-3: Process parameters utilised for increased travel speed of MES deposition of Ti-6Al-4V

ID	Laser Power (W)	Arc Current (A)	Scan Speed (mm.s ⁻¹)	Scan width (mm)	Travel Speed (mm.s ⁻¹)
TS 1	3000	140	500	6.75	2.00

From the macrographs of the central cross-sections (Figure 5-10) it may be observed that the height of the bead increased with WFS as expected. In comparison to PI 1 and PI 2, the depth of penetration appears to have decreased, alongside the size of the primary and secondary HAZ [34], which occurred due to the decreased heat input as travel speed increased. It may be qualitatively observed that the size of penetration and HAZ was of similar sizes across all specimens, regardless of WFS, and was to be expected given an equivalent heat input. The grain structure demonstrated a columnar prior- β grain morphology, which was expected as the process was not optimised for prior- β grain structure control. The geometry of the deposited bead may be observed in Figure 5-11.

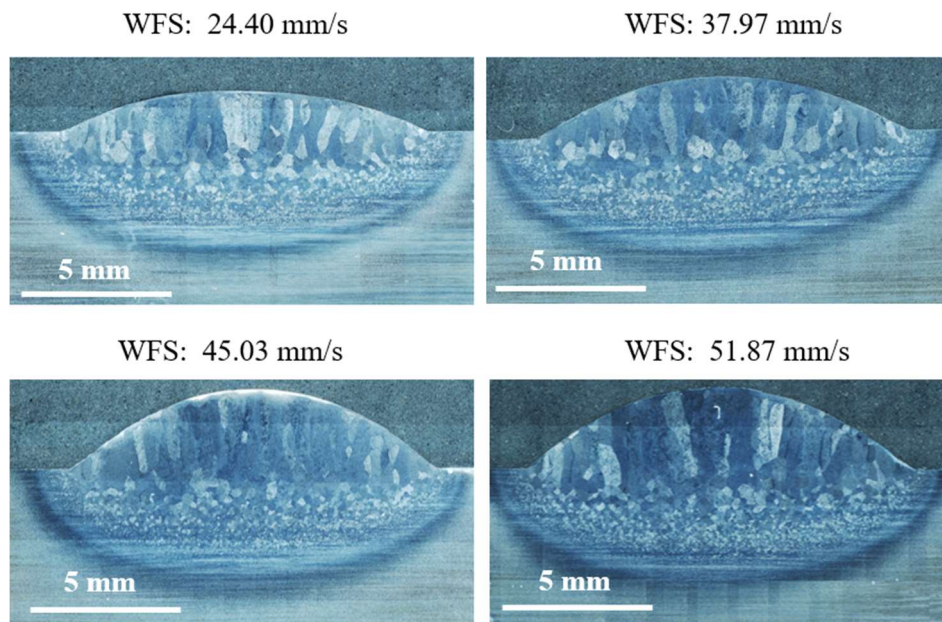


Figure 5-10: Etched cross sections of Ti-6Al-4V MES deposited specimens at varying WFS and increased travel speed.

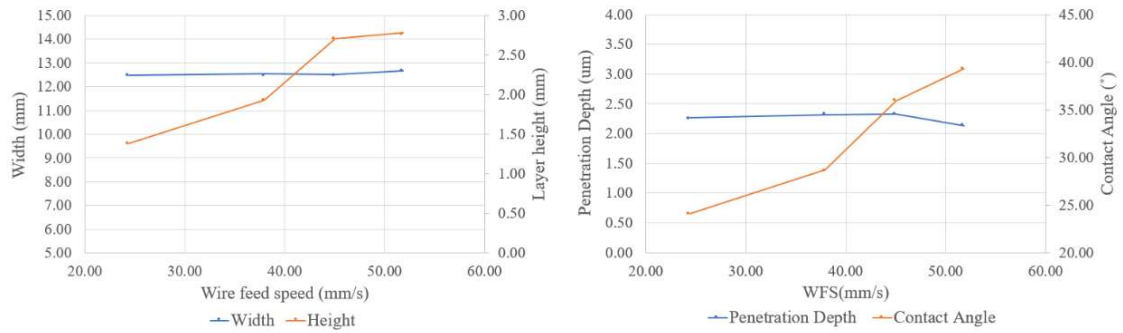


Figure 5-11: Bead geometry measurements from cross-sections increased travel speed specimens (L) Bead width and height, (R) Penetration depth and bead contact angle with substrate.

Despite the increase in travel speed to 2 mm.s^{-1} , the independent control of the bead width and bead height was maintained. The contact angle and build height were larger than the preliminary investigation specimens due to an increase in WFS and deposition rate. The depth of penetration was significantly improved in relation to the preliminary investigation, reducing to $\sim 2.25 \text{ mm}$ from $\sim 5.50 \text{ mm}$. This occurred through the increased travel speed and consequent reduction in heat input. The bead geometry measurements for the bead width and bead height of the TS 1 specimens also demonstrated alignment with the intended geometric bead shape. The bead shape control prediction (Equation 5-9) is therefore a useful tool to identify processing parameters and identify melt pool shape and bead geometry using the MES system. For example, when considering the actual bead width in place of the scanning width (until such a point where desired scan width is achieved) to predict the bead height there is strong correlation with the actual deposited height. Alternatively, when using the actual bead height to predict the bead width, the prediction is also accurate, as may be observed in Figure 5-12.

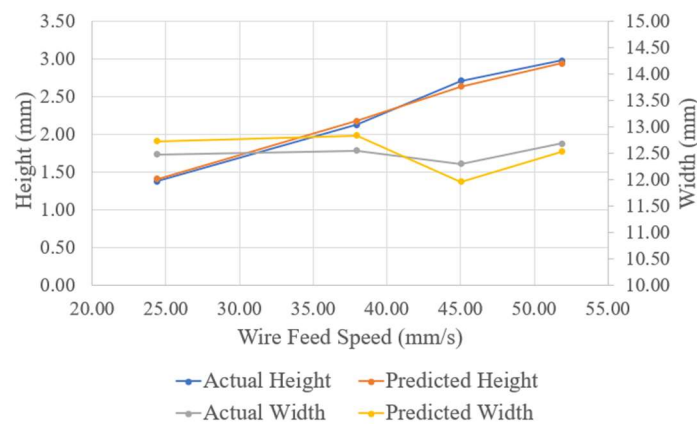


Figure 5-12: Bead geometry prediction vs actual bead deposited geometry using bead shape prediction from Equation 5-9. Note that the relationship between predicted geometry and actual geometry is closely related meaning the prediction can be used to set process parameters. In this case the scanning width has been replaced by the actual bead width.

However, the bead width remained significantly greater than the desired scan width. As discussed by previous studies [22–24], the addition of the laser energy is used to increase the size of the melt pool and in this study was responsible for generating the elongation of the melt pool. However, the specific point energy being delivered was too large and was generating a melt pool significantly larger than the desired width. Therefore, an investigation into the required specific point energy to achieve the desired scan width was required for the deposition of Ti-6Al-4V, to ensure that the melt pool shape can be controlled accurately.

5.4.3 Identification of Required Specific Point Energy

To achieve the desired scan width, the specific point energy required must be identified. During this investigation two scan widths (13.5 mm and 16.5 mm) were investigated, through the deposition of Ti-6Al-4V with fixed process parameters excluding travel speed. The travel speed was systematically increased from 3 mm.s⁻¹ to 9 mm.s⁻¹ in 1 mm.s⁻¹ increments with a WFS of 58.2 mm.s⁻¹ maintained throughout. A single line scan strategy was used at 500 mm.s⁻¹. In relation to Equation 5-2, this lowered the specific point energy delivered by the laser through a reduction in the number of interactions over a single point. Additionally, the arc current was lowered compared to the previous studies to reduce the maximum penetration depth. This allowed identification of the specific point energy required to achieved the desired bead width, without excessively overheating the substrate. The process parameters used in this study are detailed in Table 5-4 and the macrographs may be observed in Figure 5-13.

Table 5-4: Process parameters of Ti-6Al-4V samples deposited for identification of the required specific point energy to achieve desired bead width

ID	Laser Power (W)	Arc Current (A)	Scan Speed (mm.s ⁻¹)	Scan width (mm)	Wire feed speed (mm.s ⁻¹)
SE 1	3000	105	500	13.5	58.2
SE 2	3000	105	500	16.5	58.2

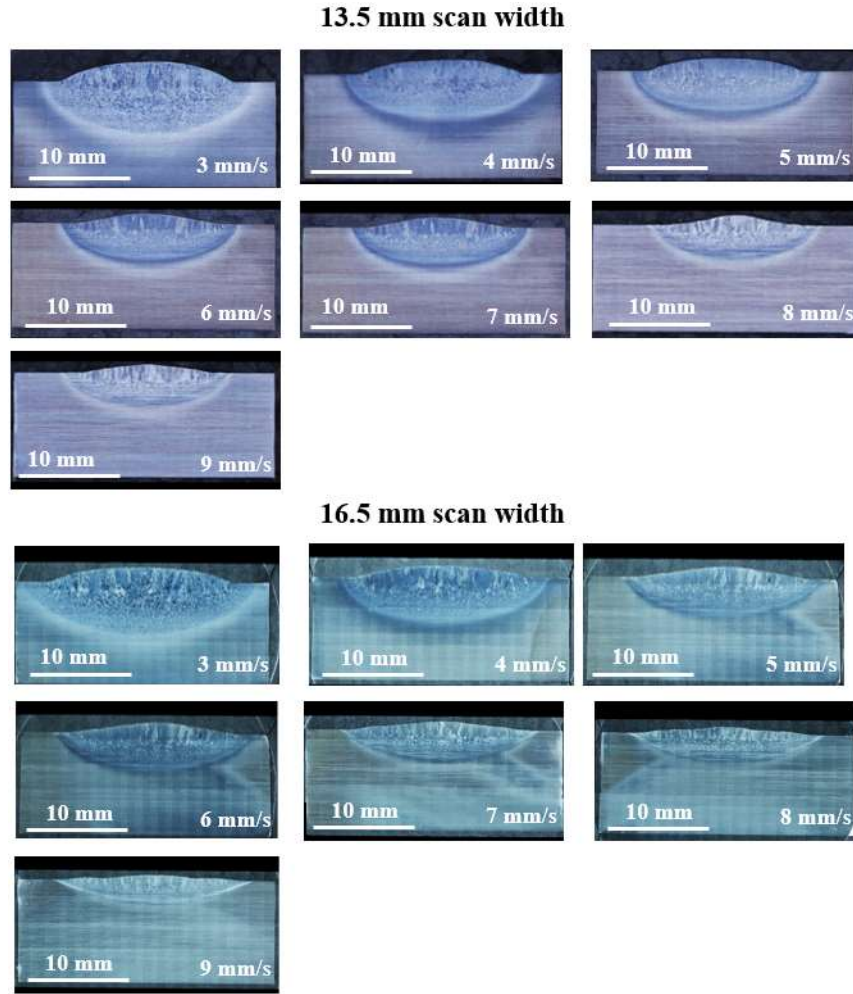


Figure 5-13: Light macrograph cross-section of etched Ti-6Al-4V deposited specimens with a reduction in specific point energy (T) Scan width = 13.5 mm (B) Scan width = 16.5 mm.

It may be observed from Figure 5-13 that, for both scanning widths as the travel speed of deposition was increased there was a distinct change in bead geometry. Most notably in the bead height, penetration depth and primary HAZ. As the WFS was fixed, the decrease in bead height was attributed to the reduction in deposition rate as the travel speed increased. The reduction in penetration depth and primary HAZ can be attributed to the reduction in heat input from the arc and lower specific point energy of the laser [23]. When the travel speed reached 8 mm.s^{-1} for the 13.5 mm scan width in SE 1, the deposited material did not appear to have fully spread and the bead shape was triangular. A comparable observation is made in the 16.5 mm scan width in SE 2 from 7 mm.s^{-1} upwards. A similar response is noted in Kapil et al. [22] where the molten material would not sufficiently spread and can be attributed to the specific point energy being too low. The bead geometry for both the SE 1 and SE 2 may be observed in Table 5-5 and Table 5-6 respectively.

Table 5-5: Bead geometry and specific point energy of SE 1 specimens

Scan width (mm)	13.50	13.50	13.50	13.50	13.50	13.50	13.50
Travel speed (mm.s ⁻¹)	3.00	4.00	5.00	6.00	7.00	8.00	9.00
Width (mm)	16.84	16.16	15.43	14.02	13.66	12.60	12.32
Height (mm)	1.96	1.42	1.28	1.01	0.91	0.85	0.79
Penetration depth (mm)	1.39	0.73	0.66	0.57	0.54	0.52	0.59
Specific point energy (J)	592.59	444.44	355.55	296.30	253.97	222.22	197.53

Table 5-6: Bead geometry and specific point energy of SE 2 specimens

Scan width (mm)	16.50	16.50	16.50	16.50	16.50	16.50	16.50
Travel speed (mm.s ⁻¹)	3.00	4.00	5.00	6.00	7.00	8.00	9.00
Width (mm)	18.70	17.72	17.07	16.78	15.94	15.72	15.44
Height (mm)	1.55	1.18	1.15	0.85	0.81	0.73	0.52
Penetration depth (mm)	1.16	1.08	0.90	0.87	0.84	0.59	0.58
Specific point energy (J)	484.85	363.64	290.91	242.42	207.79	181.82	161.62

It may be observed that as the travel speed increased, the specific point energy became lower. This was a consequence of fewer interactions with a single point as the scanning speed and width remained constant reducing the amount of energy delivered to a single point. During the deposition of the SE 1 specimens, the scan width and measured width almost converged (highlighted in bold) at 253.97 J specific point energy. The same observation can be made for the SE 2 specimens, where the scan width and bead width converged (highlighted in bold) at 242.42 J. Therefore, it may be deduced that to ensure that the control of the bead width can be achieved for a desired scan width, a specific point energy of $\sim 240 - 250$ J is required. Consequently, in relation to the bead shape prediction (Equation 5-9), the actual measured bead heights for the respective specific point energies identified corresponded to a 13.16 mm bead width for SE 1 and 16.43 mm bead width for SE 2 prediction, demonstrating a strong correlation with the actual measured bead widths of 13.50 mm and 16.50 mm respectively.

5.4.4 Reduction of Laser Energy at Scan Width Centre

As previously discussed, a significant amount of arc energy is delivered to the centre of the scan path when a single line strategy is employed. However, during the formation of the quasi-steady state melt pool between the arc and laser, there is no requirement for additional laser energy in the melt pool centre as this is provided by the arc [13]. Therefore

the removal of laser energy over the arc melt pool was investigated with equivalent process parameters to SE 1 and SE2 listed in Table 5-4 for direct comparison to the single line strategy. Three travel speeds were considered, 4 mm.s⁻¹, 5 mm.s⁻¹ and 6 mm.s⁻¹ for each scan width (13.5 mm and 16.5 mm). The scan strategy used, was equivalent to the preliminary investigation as illustrated in Figure 5-4. A 3.5 mm gap was maintained at the centre of the scan width and each side of this a 5 mm and 6.5 mm length used for the combined 13.5 mm and 16.5 mm scan width respectively. The macrographs may be observed in Figure 5-14.

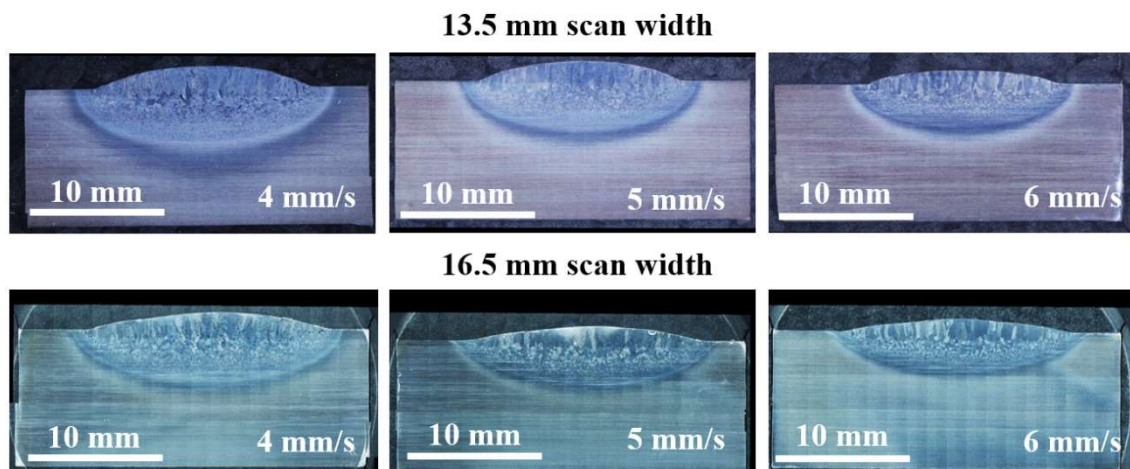


Figure 5-14: Light macrographs of etched central cross-sections of 3-line scan strategy Ti-6Al-4V deposits, utilising equivalent parameters to SE 1 and SE 2 for 13.5 mm and 16.5 mm scan width at 4 mm.s⁻¹, 5 mm.s⁻¹ and 6 mm.s⁻¹ travel speed.

No discernible qualitative difference between the specimens deposited with the 3 line scan strategy to their equivalent single line strategy from the PE 1 and PE 2 study could be seen. Quantitative analysis of the bead geometry is reported in Table 5-7 and Table 5-8, comparing the geometries of the single line strategy from SE 1 and SE 2 to the 3 line strategies in this study.

Table 5-7: Bead geometry of single line study SE 1 compared with multi 3-line strategy of equivalent process parameters at 13.5 mm scan width

Scan strategy (SL – single line 3L – 3 line strategy)	SL	3L	SL	3L	SL	3L
Travel speed (mm.s ⁻¹)	4	4	5	5	6	6
Height (mm)	1.42	1.49	1.28	1.35	1.01	1.04
Width (mm)	16.16	16.05	15.43	15.09	14.02	14.15
Penetration depth (mm)	0.73	0.78	0.66	0.72	0.57	0.62
Primary HAZ depth (mm)	2.96	3.03	2.4	2.44	2.18	2.07

Table 5-8: Bead geometry of single line study SE 2 compared with multi 3-line strategy of equivalent process parameters at 16.5 mm scan width

Scan strategy (SL – single line 3L – 3 line strategy)	SL	3L	SL	3L	SL	3L
Travel speed (mm.s ⁻¹)	4	4	5	5	6	6
Height (mm)	1.18	1.28	1.15	1.10	0.85	0.98
Width (mm)	17.72	18.04	17.07	17.01	16.78	16.95
Penetration depth (mm)	1.08	0.91	0.90	0.74	0.87	0.64
Primary HAZ depth (mm)	2.58	2.52	1.93	1.99	1.99	1.69

As may be observed, with respect to the 13.5 mm scan width, regardless of whether a single line or multi 3-line scan strategy was used, the bead geometry remained relatively consistent across the bead width, height, penetration depth and primary HAZ. Suggesting that the 3-line scan strategy had little effect on reducing heat input and did not alter the deposition characteristics significantly. In the case of the 16.5 mm scan width, a minor impact of the 3-line strategy could be noticed. In the case of bead width and bead height the geometry remained consistent. In the case of the primary HAZ, the size remained consistent until the 6 mm.s⁻¹ case where a 0.3 mm difference in HAZ could be determined. In the case of the penetration depth, a consistent ~ 0.2 mm lower penetration depth was achieved in all cases for the 3-line scan strategy, inferring that the removal of the laser energy at this point prevented a small quantity of remelting and improved process efficiency [6]. The slight reduction in penetration depth in the 16.5 mm specimens as compared to the 13.5 mm specimens may be a result of the larger melt pool surface area interaction with the substrate providing a larger area for conduction, more effectively drawing heat away from the melt pool. However, this phenomenon requires further investigation.

In summary, analysis of all the previous studies provides a fundamental understanding of melt pool geometry control of Ti-6Al-4V for the MES process proposed by Chen et al. [13]. This understanding allowed the following study to focus upon utilising melt pool geometry control to alter the prior- β grain structure of Ti-6Al-4V during MAM. As suggested by Wainwright et al. [27,30] the melt pool shape is responsible for prior- β grain structure control.

5.4.5 Prior- β Grain Structure Control of Ti-6Al-4V via MES Deposition

As discussed by Wainwright et al. [27], the effect of melt pool geometry influences the prior- β grain structure during the additive manufacturing of Ti-6Al-4V. In particular the length/depth (L/D) ratio of the deposited bead and melt pool length, providing a proxy measure of melt pool curvature. As melt pool curvature increases, this provides an opportunity for dendrite twinning during solidification which leads to the breakdown of epitaxially grown columnar prior- β grains as seen by $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ misorientations akin to known body centre cubic twinning systems $\{332\}_\beta \langle 113 \rangle_\beta$ and $\{112\}_\beta \langle 111 \rangle_\beta$ respectively. Wainwright et al. [27] have also posited the use of the specific energy density of deposited material (SED), i.e. the energy per unit volume of feedstock, as a measure for determining the prior- β grain structure. As the total energy delivered is spread across a larger volume of material, this has the potential to reduce the thermal gradient [30]. However, with the disadvantages of the single energy source, they were not able to isolate the SED from the bead geometry i.e. the L/D ratio could only be altered via a reduction in SED by increasing deposition rate. Therefore, whilst their study showed that dendrite twinning was the primary refinement mechanism responsible over nucleation ahead of the solidification front, it could not be explicitly stated whether this was a consequence of SED reduction or the increase in melt pool curvature.

Utilising the MES system, it is possible to independently control the SED from the bead geometry. Therefore, three walls were deposited with a SED of 29.50 J.mm^{-3} as calculated by Equation 5-6. This was the minimum SED achievable with the MES source, as the WFS was at a maximum of 49.92 mm.s^{-1} to maintain a stable droplet transfer mode [42]. The walls were deposited on Ti-6Al-4V substrates (12 mm x 100 mm x 25 mm), the samples being deposited on the short edge of the substrate to mimic conduction losses otherwise seen as the thermal mass changes when depositing a wall from a flat substrate [30]. This allows for fewer layers to be deposited for analysis. Approximately 20 mm of Ti-6Al-4V was deposited for each of the walls using a sawtooth scan strategy as demonstrated in Figure 5-15, of a fixed 11 mm scan width and 1 mm, 5 mm and 10 mm amplitudes. To ensure a specific point energy of $\sim 250 \text{ J}$, (as determined previously – SE specimen study above) to achieve the desired scan width, the scanning velocity was

increased with the amplitude to maintain a scan frequency of 20 Hz across all three specimens. The remaining process parameters are presented in Table 5-9.

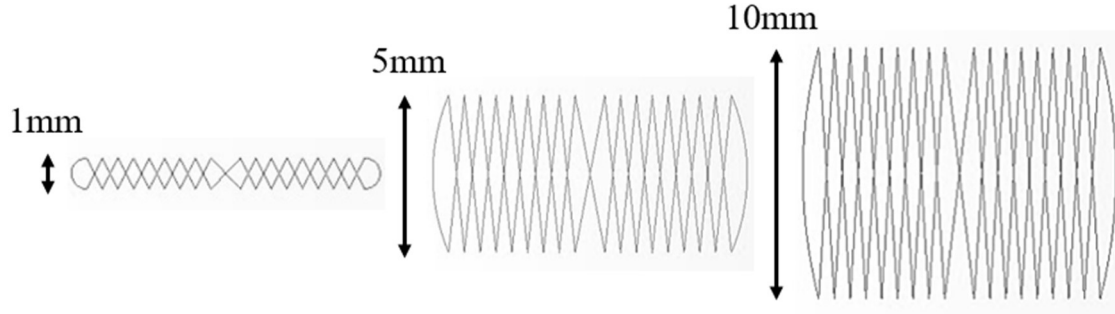


Figure 5-15: Laser scan path strategy for 1 mm, 5 mm and 10 mm oscillation with 11mm scan width.

Table 5-9: Deposition parameters of MES grain structure control study

ID	Scan amplitude (mm)	Laser Power (W)	Arc Current (A)	Scan Speed (mm.s ⁻¹)	Travel speed (mm.s ⁻¹)	Wire feed speed (mm.s ⁻¹)
A1	1	1500	105	1600	4	49.92
A5	5	1500	105	5700	4	49.92
A10	10	1500	105	15000	4	49.92

In comparison to the PTA only SED specimens deposited by Wainwright et al. [27], the combination of the arc and laser in the MES process was somewhat limited by the combined total energy required for deposition. As described by Wang et al. [23], where the PTA was used to melt the wire, this MES process operated in a similar fashion with the laser trailing the PTA. Therefore, the WFS was limited by the PTA energy, which was equivalent to the single energy source study. Consequently, the SED in this study was minimised, however, it was equivalent to the SED that generated a mixed prior- β grain morphology in the Wainwright et al. [30] study. With this limitation, a refined prior- β grain structure was not expected and the purpose of this study was to observe an indication that the prior- β morphology was changing with melt pool elongation, as bead geometry would be fixed and an increase in L/D ratio would occur from the elongation of the melt pool. It was expected that a mixed refined and columnar prior- β grain structure would transform to predominantly columnar.

The effect of the 1 mm, 5 mm and 10 mm scan path amplitude on melt pool shape may be observed in the images captured during deposition, illustrated in Figure 5-16 using the Xiris XVC-1100 processing camera. It may be observed that as the scan amplitude

increased, the melt pool length also increased as expected. As previously discussed, the melt pool shape remained ovular in nature, however, extended further than the scanning amplitude. The melt pool lengths measured corresponded to a total length of 12.53 mm for the 1 mm scan amplitude, 17.58 mm for the 5 mm scan amplitude and 22.38 mm for the 10 mm scan amplitude. Therefore, all maintained the difference in scan amplitude in melt pool length. Once deposited, a longitudinal sample, machined to the central plane was taken from the central section of each specimen. Each sample was subject to EBSD analysis and prior- β grain reconstruction to determine if refinement had occurred and controlled by the L/D ratio. The prior- β grain reconstructed maps, with inverse pole figure (IPF) colouring relative to the build direction and respective L/D ratio may be observed in Figure 5-17.

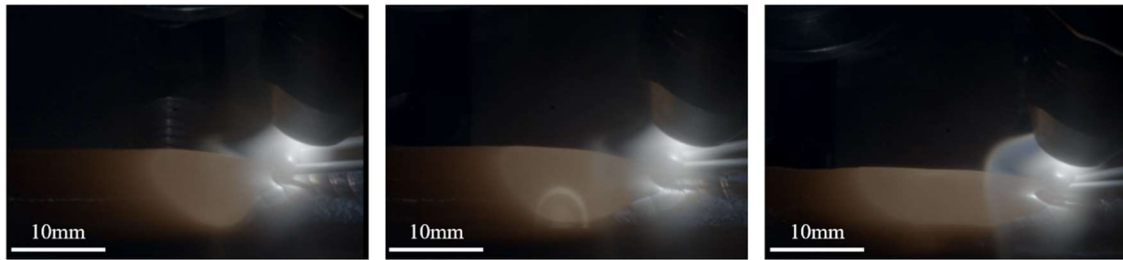


Figure 5-16: Xiris camera stills of melt pool shape during deposition of MES Ti-6Al-4V with increasing scanning amplitude a) 1 mm b) 5 mm and c) 10 mm.

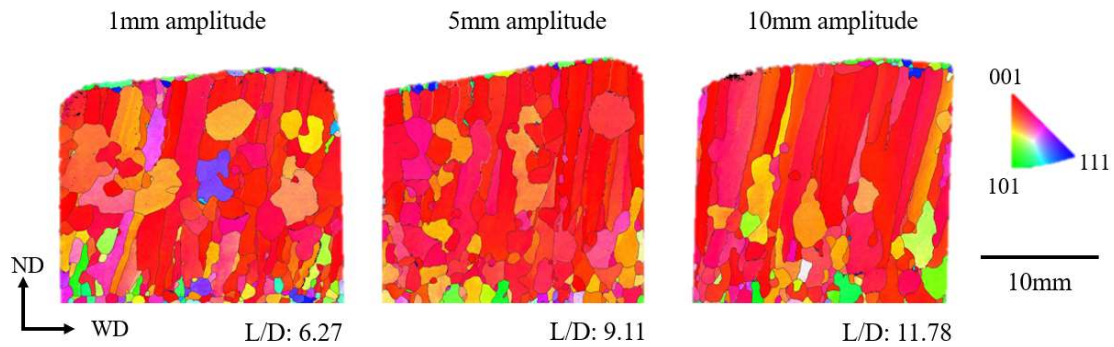


Figure 5-17: Prior- β grain reconstruction of melt pool shape during deposition of MES Ti-6Al-4V with increasing scanning amplitude a) 1 mm b) 5 mm and c) 10 mm.

In all specimens the prior- β grain structure deposited was heavily orientated with the build direction as may be observed by the red IPF colouring relative to the build direction indicating a strong $\langle 100 \rangle_{\beta}$ prior- β grain orientation. However, there was an increase in intensity as the L/D ratio increased, confirmed in the pole figures of Figure 5-18. In the case of the 1 mm specimen at 6.27 L/D ratio the morphology was as expected from Wainwright et al. [27], with a mixed prior- β grain morphology evident, however a strong texture was retained. As the L/D ratio increased to 9.11, a mixed morphology was

partially retained, however, it began to show a propensity towards a columnar morphology. In the 11.78 L/D ratio the mixed structure had been replaced by a columnar dominant structure with fewer refined grains present.

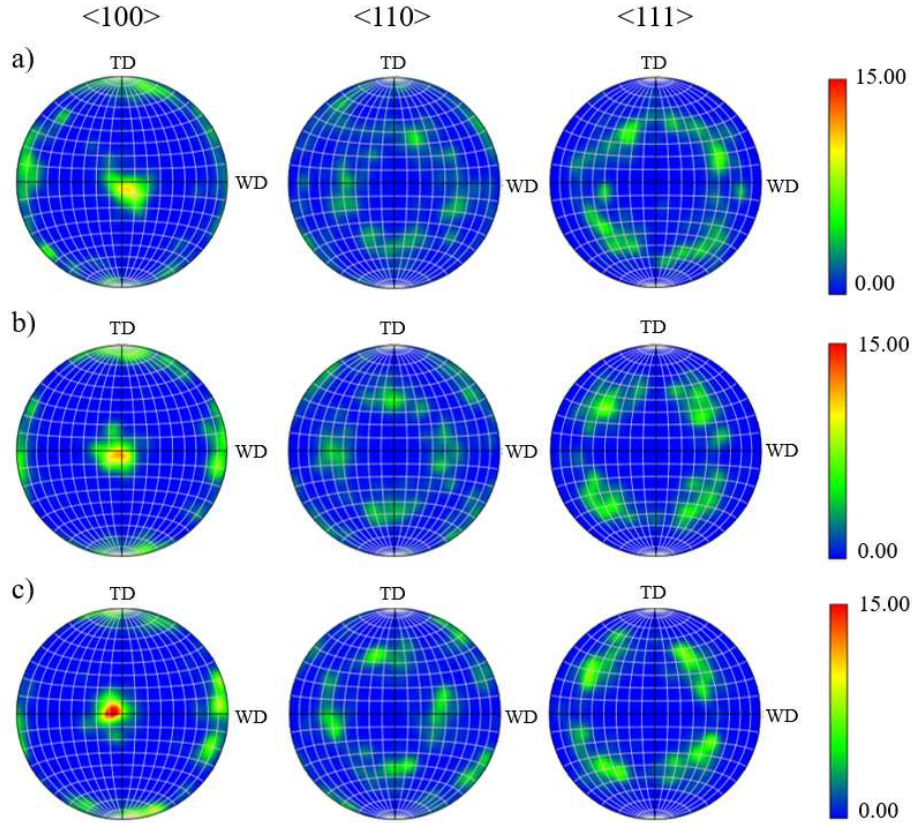


Figure 5-18: Cubic pole figures for grain structure control specimens with equivalent SED at a) 1 mm scan amplitude b) 5 mm scan amplitude and c) 10 mm scan amplitude.

The partially retained refined grains when the L/D was 9.11 and less so in the 11.78 L/D ratio specimens was unexpected given this showed an entirely columnar prior- β grain structure according to Wainwright et al. [27]. The retention likely occurred due to the interruption of the typical fluid flow within a single energy heat source melt pool and thermal gradient as seen by Gong et al. [21] and Ma et al. [19], who observed a refinement in grain structure during oscillated laser-arc hybrid induced by the stirring effect of the laser on the melt pool flow. However, the effect of stirring on Ti-6Al-4V is not as prominent, otherwise refined grains with a weak texture would dominate. Additionally, it is worth noting that the stirring effect is present across all specimens and therefore cannot be the reason behind refinement. The $\langle 100 \rangle_{\beta}$ preference was related to the combined energy input of the laser and arc where the heat input of the MES system was higher than that of the single source PTA deposition of Wainwright et al. [27] undoubtedly increasing

the thermal gradient [43]. This provided the prior- β grains gain an advantage to the easy growth $\langle 100 \rangle_\beta$ direction [44]. Despite being overly columnar, the effect of melt pool shape on the prior- β grain structure may be observed. Where the SED of deposited material and deposition rate remained constant and only the melt pool geometry altered, there was a breakdown of a mixed prior- β grains morphology to a columnar dominant morphology as the L/D ratio was increased.

As demonstrated by Wainwright et al. [27], as the L/D ratio is increased the number of $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ misorientations should decrease. Considering the misorientation distributions for the three specimens in Figure 5-19, it may be observed that whilst a large proportion of 60° misorientations exist, they are steadily declining as L/D was increased, from the 1 mm scan amplitude to the 10 mm amplitude. 60° misorientations decreased by $\sim 33\%$ and 51° misorientations by $\sim 50\%$, whilst the cumulative number of $< 10^\circ$ low angle grain boundaries typical of WAAM increased by $\sim 88\%$, confirming the hypothesis first posited by Wainwright et al. [27]. Further investigation is required to achieve a fully refined equiaxed prior- β grain structure as seen by Wainwright et al. [27,30], however, in principle the MES system proposed by Chen et al. [13] is capable of altering the grain structure of Ti-6Al-4V via melt pool shape control.

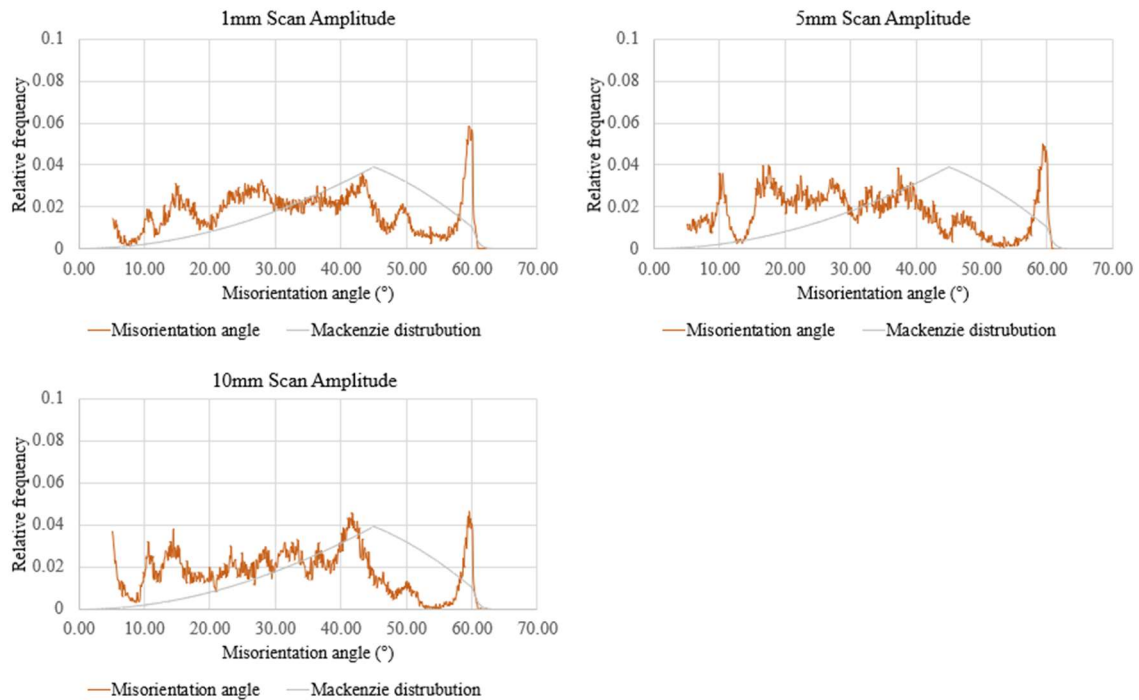


Figure 5-19: Misorientation angle distribution of 1 mm, 5 mm and 10 mm scan amplitudes for fixed SED and heat input.

When considering the effect of the melt pool shape on the prior- β grain morphology, the level of refinement can be determined by the aspect ratio of the prior- β grains. As may be observed in Figure 5-20, the aspect ratio of the grains increased from the 1 mm scan amplitude specimen to the 10 mm specimen. It may be seen for the 1 mm scan amplitude specimen that the aspect ratio was dominated by < 2.0 aspect ratio prior- β grains and few > 3.0 aspect ratio prior- β grains. As the scan amplitude and L/D increased, for the 5 mm scan amplitude, a large proportion of < 2.0 aspect ratio prior- β grains existed, however, a larger proportion of > 5.0 aspect ratio grains appeared. In the 10 mm scan amplitude specimen, a large proportion of ~ 2.0 and ~ 4.0 aspect ratio prior- β grains existed, as well as ~ 7.75 aspect ratio grains. This indicated the increasing level of columnar prior- β grains as L/D increased with scan amplitude.

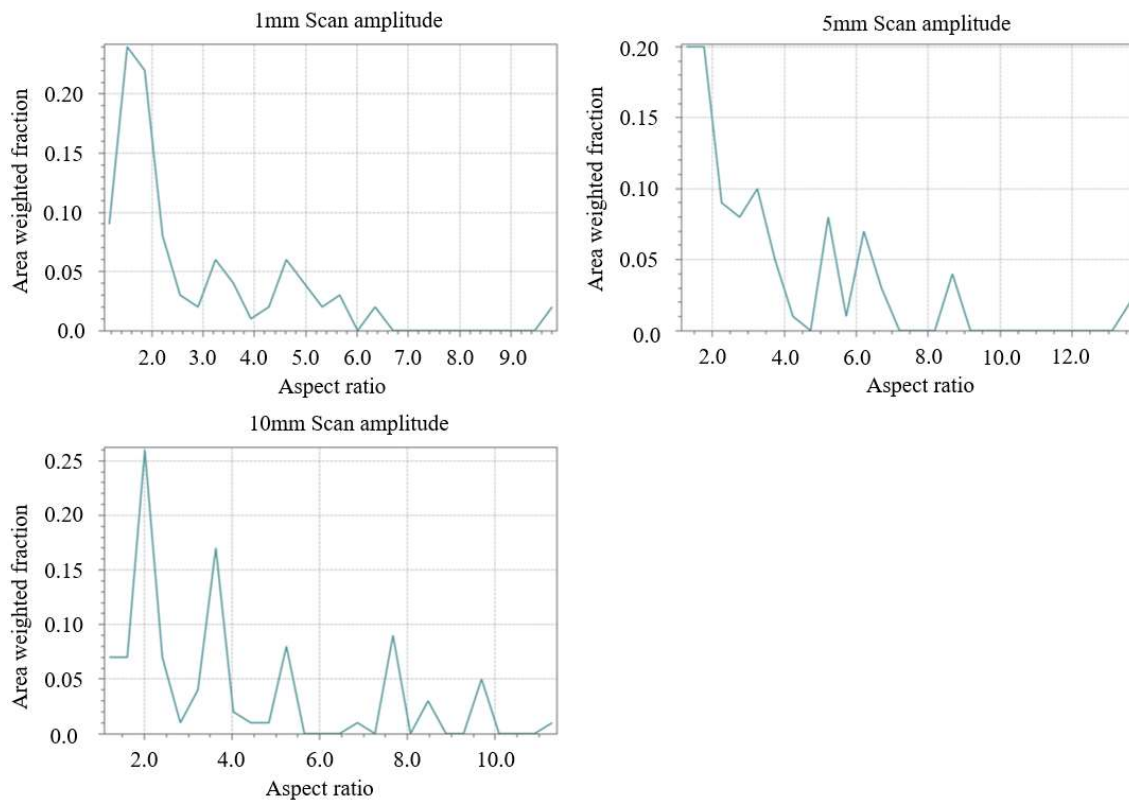


Figure 5-20: Aspect ratio of prior- β grains as a function of area weighted fraction for 1 mm, 5 mm and 10 mm scan amplitude.

Whilst the deposited specimens were not large enough to extract tensile specimens to consider the mechanical performance, microhardness measurements by Vickers method were conducted. It was expected that as the equivalent total energy input, SED and deposition rate across the specimens remained constant, an equivalent cooling rate would be obtained and therefore the microhardness would be equivalent [15]. The

microhardness values for the three specimens may be observed in Figure 5-21. The average hardness for the 1 mm, 5 mm and 10 mm scan amplitude specimens was $349.36 \text{ Hv} \pm 17.82$; $355.67 \text{ Hv} \pm 12.48$ and $349.30 \text{ Hv} \pm 17.56$ respectively. It can be determined therefore, that the α microstructural characteristics of the specimen were similar, as the inter-lamellar spacing (ILS), thus effective slip length, has been demonstrated to be inversely proportional to the hardness [45,46]. This confirmed that from the equal heat input, an equivalent cooling rate between the specimens was maintained, as hardness has been demonstrated to vary with heat input [14,15].

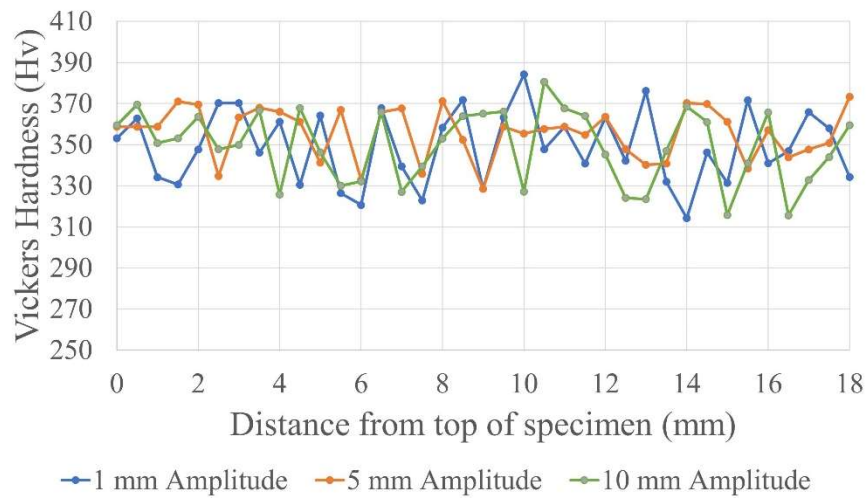


Figure 5-21: Vickers microhardness of 1 mm, 5 mm and 10 mm scan amplitude specimens measured from the top of deposit.

5.5 Conclusions

The outcomes of this study demonstrated that the laser-arc MES proposed by Chen et al. [13] used to deposit mild steel, is applicable to the deposition of Ti-6Al-4V for the purpose of additive manufacturing. This process allowed configuration of the melt pool shape and was demonstrated to be independent of the thermal input to allow investigation of the prior- β grain structure control of Ti-6Al-4V. Whilst a high heat input led to the formation of $\langle 100 \rangle_{\beta}$ textured prior- β grains, a change in grain structure morphology was observed as melt pool shape was elongated and L/D ratio increased as observed by Wainwright et al. [27] for single energy source deposition. However, in this study a fixed specific energy density of deposited material was maintained and fixed specific point

energy that allowed the L/D ratio to be isolated from the SED as per the previous limitation of the study by Wainwright et al. [27].

In summary:

- 1) Utilising a scanning laser MES process to manipulate melt pool shape, the independent control of melt pool shape, thus, bead geometry control, was obtained independently of the thermal input for the deposition of Ti-6Al-4V.
- 2) The specific point energy required to deposit Ti-6Al-4V allowing the material to spread correctly during the MES deposition was identified. At values above the required specific point energy the bead width was greater than the desired scan width, lower than required specific point energy and the material would not spread.
- 3) The penetration depth and primary HAZ at the centre of the scanning path can be manipulated through the removal of laser energy via a multi-speed scan strategy, increasing scan speed at the scan path centre and improving process efficiency.
- 4) Prior- β grain structure of Ti-6Al-4V can be altered through manipulation of the melt pool length independent of thermal input, through the manipulation of melt pool length/depth ratio.
- 5) The large heat input generated through the combination of energy sources provided a growth advantage to $\langle 100 \rangle_{\beta}$ prior- β grains, generating strong texture within the deposited specimens.

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6. Summary and Conclusions

6.1 Summary

The aim of this research was to investigate the columnar-to-equiaxed transition of the prior- β grain structure during the deposition of a wire + arc additively manufactured titanium alloy in the as-deposited condition, whilst concurrently identifying the mechanism of refinement. A systematic set of objectives were set to achieve this aim and have been successfully achieved. The initial hypothesis considered a traditional solidification theory-based approach in the lowering of the thermal gradient, to increase the potential for constitutional supercooling and induce nucleation ahead of the solidification front.

A traditional approach was adopted for the deposition of Ti-6Al-4V in Chapter 3, whereby, the increase in wire feed speed (WFS), as a variable performance parameter during Wire + Arc Additive Manufacturing (WAAM) for a fixed arc energy and travel speed, was investigated. It was proposed that a new measure, the specific energy density of deposited material (SED), could be used to account for the energy per unit volume of feedstock material. Utilising pyrometry, it was determined that the linear thermal gradient approximation across the deposits decreased as the SED reduced. Consequently, this led to the development of prior- β grain refinement that in the initial high SED specimens manifested as the typically observed columnar prior- β grains, before transformation into a columnar and refined prior- β grain mixture, and ultimately a refined prior- β grain structure as the SED lowered. As a result of the refined prior- β grain morphology, the $\langle 100 \rangle_{\beta}$ crystallographic texture had significantly weakened. However, an optimal SED value was discovered, as for the lowest SED specimen, a tilt towards the deposition direction occurred, with the prior- β grains obtaining a growth advantage.

An investigation of the grain boundary misorientations highlighted that whilst the grains began to follow the Mackenzie distribution for a random polycrystalline material, indicating nucleation ahead of the solidification front as SED reduced, distinct 51° and 60° misorientation peaks developed. This inferred that another refinement mechanism may be responsible for prior- β grain structure refinement. This was first considered with respect to melt pool temperature as the SED reduced. Investigation determined that

reduction in thermal gradient did not occur as a result of a drop in melt pool temperature, instead, the feedstock transfer mode was responsible for the melt pool temperature as a result of arc shading when WFS was increased. The reduction in thermal gradient was a consequence of the increase in deposition height, indicating the melt pool shape may be a factor in prior- β grain structure morphology and the tilting of the prior- β grains in the lowest SED specimen. This prompted an investigation into the effect of melt pool shape as discussed in Chapter 4.

Several thermal profiles and titanium alloys were considered within Chapter 4, to test the validity of the SED hypothesis and to determine whether melt pool shape was a prior- β grain structure control method. Several studies were considered at equivalent SED values to those utilised in Chapter 3. Initially, the travel speed of deposition was reduced to decrease the solidification velocity, theoretically making prior- β grain refinement harder to achieve. However, the refinement occurred at an equivalent rate to the Chapter 3 study and in the lowest SED case fully horizontal orientated prior- β grains had formed without texture. In between these long horizontally orientated prior- β grains were fine and highly textured grains in line with the build direction. The following study maintained the SED and travel speed in relation to the Chapter 3 study, whilst using an increased arc energy and WFS to alter the process conditions and melt pool shape. Although prior- β grain refinement was achieved, it occurred at a slower rate than the Chapter 3 study with columnar prior- β grains retained at lower SED values. This demonstrated that the prior- β grain morphology was not primarily determined by the SED and therefore the mechanism of refinement may not have been related to traditional solidification theory as the thermal gradients and alloy composition were equivalent.

Consequently, Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-Mo-5V-3Cr were selected for their increasing percentage of molybdenum, which demonstrates high growth restriction in titanium and therefore would increase the available constitutional supercooling. Theoretically, it was considered that this would lead to refinement occurring at higher values of SED, as if nucleation ahead of the solidification front was the dominant mechanism, this would occur more easily with the available constitutional supercooling increase. In the case of Ti-6Al-2Sn-4Zr-2Mo, the overall prior- β grain structure morphology was finer than the Ti-6Al-4V, however, refinement occurred at an equivalent rate. In the case of Ti-5Al-5Mo-5V-3Cr, very little refinement occurred and only at the

lowest SED was some evidence of refinement obtained. This clearly demonstrated that nucleation ahead of the solidification front was not the dominant refinement mechanism. Instead, further consideration of the grain boundary misorientations in all cases highlighted the same evolution of 51° and 60° misorientations as prior- β grain refinement occurred. Through electron back-scattered diffraction (EBSD) analysis, it was determined that these existed as $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ misorientations and are akin to known body centre cubic twinning systems $\{332\}_\beta \langle 113 \rangle_\beta$ and $\{112\}_\beta \langle 111 \rangle_\beta$ respectively. This indicated that dendrite twinning during solidification was primarily responsible for prior- β grain refinement rather than nucleation ahead of the solidification front. In order to achieve a stacking fault to enable twinning, it was posited that as β grains grow in line with the maximum thermal gradient perpendicular to the solidification front, as the melt pool curvature increased this would develop strain and induce dendrite twinning. Consideration of all deposited samples from both Chapter 3 and Chapter 4 in terms of the melt pool length/depth (L/D) ratio, a proxy measure of curvature, was conducted. The results highlighted that prior- β grain structure and L/D ratio were connected, with an L/D ~ 4.0 being the optimal configuration, > 6.0 a columnar morphology was observed and < 4.0 a tilt towards the deposition direction was observed. In the case of Ti-6Al-2Sn-4Zr-2Mo, the melt pool shapes were similar to the Ti-6Al-4V, hence, the equivalent rate of refinement. For the Ti-5Al-5Mo-5V-3Cr specimens, the melt pool length was significantly longer leading to a higher L/D ratio, therefore, confirming why minimal refinement was obtained. In the lowest SED specimen of the Ti-5Al-5Mo-5V-3Cr specimens, a L/D ratio of ~ 6.0 was obtained and this showed an equivalent level of refinement to the Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo specimens of equivalent L/D ratios. However, the limitation of the study was intrinsic to single source energy deposition. The bead geometry was dependent on the process parameters and cannot be isolated from them. Therefore, melt pool shape and SED were both changing simultaneously. To isolate the melt pool shape from the thermal input, a multi-energy source (MES) process to independently control bead geometry from the thermal input was considered.

In Chapter 5, the applicability of an MES process was considered for deposition of Ti-6Al-4V. The ultimate purpose of the study was to maintain the SED and deposition process parameters whilst manipulating the bead geometry to alter the melt pool shape

and consider the effects on prior- β grain structure. The MES process utilised a plasma arc to generate an initial melt pool and melt the feedstock wire, whilst a trailing laser scanning from side to side would cause the material to spread across a desired scan width. By ensuring the same specific point energy of the laser source, the energy input remained consistent. It was demonstrated that bead width and bead height could be independently controlled via the WFS and scan width settings respectively. After a preliminary investigation, an excessive heat input meant that the bead width obtained was significantly higher than the desired scan width. Therefore, an investigation into optimising the process parameters was conducted. The specific point energy required to accurately deposit the desired scan was determined. A specific point energy that was too large would lead to a bead width greater than desired scan width, too low and the melt pool flow was insufficient such that the melt pool would not spread. Once optimised a 'sawtooth' scan strategy with multiple scan amplitudes was used to investigate the effect of L/D ratio on the prior- β grain structure morphology. This allowed the bead height to be fixed and only melt pool length altered. Results demonstrated success in elongating melt pool length to increase the L/D ratio but also demonstrated a transformation from a mixed grain structure to predominantly columnar, thus highlighting the limitation of the MES system. In the configuration applied, the combined energy input of the arc and laser led to the formation of a mixed rather than refined prior- β grain structure in the first instance rather than a fully refined one as demonstrated in Chapter 3 and Chapter 4. This is in part due to the limitation of only the plasma arc being used to melt the feedstock wire. The maximum WFS obtainable was equivalent in a single arc process to the MES process at equivalent arc energy inputs, as only the arc is melting the wire. The MES system will therefore always incur a higher energy input for the maximum obtainable deposition rate to the detriment of grain structure and texture as observed.

Overall, the successful refinement of the prior- β grain structure of titanium alloys has been successfully demonstrated in the as-deposited condition whilst maintaining a stable processing condition. Unlike, previous research there is no reliance on mechanical working, melt pool agitation or inoculation. The research has identified a new method of obtaining prior- β grain refinement in the form of dendrite twinning. The research aim and objectives have been fulfilled, ultimately providing a new avenue for grain refinement during titanium alloy deposition during WAAM and closing the research gap identified.

6.2 Future Work

Whilst this research has demonstrated the ability to obtain prior- β grain refinement in the as deposited condition for several titanium alloys deposited with WAAM, several avenues of investigation should be considered to continue this research. Primarily, further focus on theoretical understanding of the refinement mechanism through the use of modelling and subsequent optimisation of the processes used to achieve refinement to realise commercial benefits.

6.2.1 Modelling

To fully characterise the effect of melt pool curvature and its effect on prior- β grain structure requires fluid flow modelling to fully understand the melt pool shape throughout deposition. With a full understanding of the melt pool curvature at various points within the melt pool, the effect of melt pool shape manipulation can be better utilised and understood. Additionally, this should be coupled to finite element analysis to categorise the local strain as the melt pool curvature is changing, this would allow further investigation and confirmation of the dendrite twinning hypothesis. If fluid flow modelling could be coupled with the ability of the multi-energy source process to manipulate melt pool shape this would allow design of localised prior- β grain structure control.

6.2.2 Localised Grain Structure Control

The ultimate benefit of the as-deposited prior- β or β grain structure control of titanium alloys is the ability to localise the grain structure. It is well known that the grain structure dictates the mechanical response observed in materials. Utilising additive manufacturing to alter the grain structure locally, allows for the configuration of mechanical properties at distinct points. For a design engineer this would add even greater design freedom than typically gained during additive manufacturing. This work has focused on the fundamental mechanisms of obtaining prior- β and β grain refinement and as such deposited only homogenous grain structure morphologies. Consideration should be given to alternating the melt pool shape at discrete points to test the viability of localising grain structure and subsequent mechanical testing to characterise the benefits of prior- β grain structure control in the as-deposited condition.

6.2.3 Increased Deposition Rate using Multi-Energy Source System

The preliminary investigation of the multi-energy source scanning laser and arc process demonstrated that the control of grain structure can be achieved, albeit in a limited fashion. Having identified that the length/depth ratio is a controlling factor of prior- β grain structure, an investigation to overcome the limitations of the single energy source wire melting is required. The reliance of the arc to melt the feedstock limits the deposition rate equivalent to a single energy source deposit. Therefore, to achieve a fully refined prior- β grain structure in Ti-6Al-4V using the multi-energy source process a larger deposition rate is required to achieve the correct length/depth ratio. One such method is induction heating to increase the feedstock pre-melting temperature, this would require less energy from the arc to be melted and thus an increase in deposition rate and decrease in length/depth ratio conducive to refinement could be achieved. This would provide greater flexibility over the melt pool shape design and thus lead to greater prior- β grain refinement, enlarging the process window, which at present is restrictive. Additionally, further investigation to optimise the processing parameters should be undertaken, for example the beam diameter and laser scanning path.

6.2.4 Mechanical Testing

This research has focused on achieving prior- β grain refinement in the as-deposited condition and the underlying mechanisms. Whilst some mechanical property information was extracted through microhardness testing further investigation into the tensile and fatigue properties should be conducted. The deposition size was limited during this research due to both equipment constraints and deposition stability as surface roughness increased dramatically when prior- β grain refinement was achieved. It is well known from existing literature that refinement of the prior- β grain morphology and weakening of texture removes anisotropy inherent to WAAM titanium deposition. Utilising the benefits of the multi-energy source in stabilising melt pool shape, once optimisation of the multi-energy source system has been conducted and full prior- β grain refinement achieved, several samples should be deposited with a columnar and refined prior- β grain structure to allow extraction of tensile and fatigue samples for direct comparison and characterisation of mechanical properties.

6.2.5 Application to Medium-Large Scale Additive Manufacturing

During this research only simple wall geometries have been considered during deposition. However, in order for the full commercial benefits of this research to be implemented, investigation into large scale deposits is required. Additionally, complex geometries should be considered that involve complex features such as intersections where the thermal mass is changing, as well as differing deposition strategies such as oscillated and parallel pass. The latter is particularly important for the continuous deposition of additively manufactured components built in a reasonable time frame. Additional processes should be considered over plasma transferred arc, in particular the application of grain structure control for the cold-wire MIG process, which generates high deposition rates but suffers from poor shape fidelity. The benefits of as-deposited grain structure control and high deposition rate would be a large step in titanium additive manufacturing.

6.3 Conclusions

In this research, to investigate the columnar-to-equiaxed transition of the prior- β grain structure during the deposition of a wire + arc additively manufactured titanium alloy in the as-deposited condition, the major findings may be summarised as:

1. During the single energy source deposition of Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr, the prior- β and β grain structure can be refined from the typically observed textured columnar grain structure to a refined grain structure with weak texture via a reduction in the melt pool length/depth ratio.
2. When the length/depth ratio is decreased past an optimum, grain growth in the deposition direction gains a growth advantage resulting in horizontally orientated grains.
3. A reduction in the specific energy density of deposited material does not result in a reduction of melt pool temperature. Instead, melt pool temperature is determined by the proportion of arc shading as a consequence of the feedstock transfer mode.
4. Nucleation ahead of the solidification front as the specific energy density of deposited material is not primarily responsible for the refinement of prior- β or β grains during the as-deposited condition of titanium alloys. Grain boundary misorientations of $51^\circ \langle 110 \rangle_\beta$ and $60^\circ \langle 111 \rangle_\beta$ manifest as grain refinement

occurs, indicative of $\{332\}_{\beta} \langle 113 \rangle_{\beta}$ and $\{112\}_{\beta} \langle 111 \rangle_{\beta}$ dendrite twins during solidification as the primary refinement mechanism when melt pool curvature is increased.

5. A multi-energy source scanning laser and arc process can be used to independently control bead geometry from the thermal profile and bead geometry predicted using an ovular bead shape control theory, derived from the deposition rate in terms of volume of deposited material and cross-sectional area, to identify processing parameters required to deposit a specific shape.
6. A multi-energy source process can be used to alter the prior- β grain structure of Ti-6Al-4V during deposition for a fixed set of deposition parameters. Alteration of the melt pool shape to control the length/depth ratio of the deposit was demonstrated to alter the prior- β grain morphology obtained. This demonstrated the multi-energy source process capabilities to control bead geometry, thermal input and grain structure independently during deposition of Ti-6Al-4V.

Overall, this research presents a major impact on the application for the future of WAAM technology, with the intellectual contribution and impact of the research demonstrating:

- A novel method for refining the as-deposited grain structure of Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-5Al-5Mo-5V-3Cr through the control of melt pool shape during WAAM to facilitate dendrite twinning during solidification.
- The discovery of a previously unseen mechanism of refinement for titanium alloys deposited with WAAM process, impacting the fundamental understanding of titanium microstructural behaviour during welding and additive manufacturing.
- The ability to manipulate bead geometry and thermal field independently during deposition with WAAM, allowing customisation of bead profile for specific applications.
- The control of prior- β grain microstructure in the as-deposited condition for a fixed energy input through the manipulation of melt pool shape allowing the ability to tailor microstructure locally.

The implications of this research are significant and hold the potential for revolutionising WAAM deposition of titanium alloys. The ability to localise microstructure and thus mechanical properties seemingly at will is within the grasp of an Additive Manufacturing

Engineer. This would allow not only the deposition of components with high geometrical fidelity but also with localised mechanical performance, allowing a new class of components to be deposited.