



ARMANDO ENRIQUE CABALLERO RAMOS

Effect of different shielding conditions, thermal cycles and post-deposition treatments on melting behaviour and mechanical properties of additively built components.

SCHOOL OF AEROSPACE, TRANSPORT AND
MANUFACTURING

Welding and Additive Manufacturing Centre

PhD

Academic Year: 2022 - 2023

Supervisor: Dr Wojciech Suder

Associate Supervisor: Prof. Stewart Williams

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ABSTRACT

Additive manufacturing (AM) offers many advantages as compared to traditional manufacturing routes such as machining and forging thanks to its capability of reducing lead times, enhanced design flexibility and material saving. However, many challenges still must be overcome before this relatively novel technology can be implemented in the production of critical components. It is known that to achieve satisfactory performance of additively built parts it is important to ensure the absence of volumetric defects such as pores and the presence of a suitable microstructure that will offer the required mechanical properties. Many process variables such as shielding gas composition, thermal histories and post-deposition heat treatments can control these aspects. This work, focuses on the role of shielding gas composition on melting behaviour during laser powder bed fusion and on the microstructural evolution of stainless steel and the effect of different thermal cycles on two age hardenable alloys during Wire and Arc Additive Manufacture deposition. The objective of this thesis was to investigate how critical these variables can be in achieving the desired properties of 3D-printed parts for specific processes and alloys. The material interaction with the AM heat source is a complex phenomenon and for this reason, a wide range of advanced characterisation techniques were used in this work including high-speed imaging, scanning electron microscopy, chemical analysis, fractography, electron back-scattered diffraction, among others. It was possible to conclude that shielding gas composition is key to ensuring stability during laser powder melting of stainless steel. Additionally, the sensitivity of the microstructural features to different thermal cycles inherent to the Wire and Arc Additive Manufacture (WAAM) process was established for two age-hardenable alloys, 17-4PH (martensitic stainless steel) and Ti-5553 (near β titanium alloy). The effectiveness of standard post-deposition heat treatments to optimise the final mechanical properties of these two alloys was also identified. Finally, it was also possible to find how sensitive the developed microstructure of WAAM Ti-6Al-4V is to different levels of interstitial elements concentration. This is of great use for further applications as the incorporation of oxygen and its potential adverse effect

on mechanical performance remains one of the main concerns for the processing of titanium alloys.

Keywords:

Laser powder bed fusion, 17-4PH, Ti-5553, Wire and Arc Additive Manufacture, Ti-6Al-4V.

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LIST OF ABBREVIATIONS

AD	As deposited
AM	Additive Manufacture
BCC	Body-centered cubic
CMT	Cold metal transfer
DED	Direct energy deposition
EBSD	Electron backscattered diffraction
FZ	Fusion zone
GB α	Grain boundary alpha
GTAW	Gas tungsten arc welding
HAZ	Heat affected zone
HCP	Hexagonal close packed
L-PBF	Laser powder bed fusion
PFZ	Precipitates free zones
PTA	Plasma transferred arc
PWHT	Post welding heat treatment
SEM	Scanning electron microscope
SLM	Selective laser melting
ST	Solution treatment
TIG	Tungsten inert gas

TS	Travel speed
WAAM	Wire and arc additive manufacture
WAMC	Welding and Additive Manufacturing Centre
WFS	Wire feed speed

1 Introduction.

1.1 Research background.

Additive manufacturing (AM) of metallic alloys has become popular in the last decade as it provides an alternative manufacturing route to traditional methods such as machining, casting and forging. Initially conceived for rapid prototyping, the clear advantages of additive technologies such as material saving, design flexibility and lead times reduction have made this area receive increasing research attention. Various metal additive processes are available, depending on the heat source and feedstock utilised. Every AM technology can be broken down into three basic elements. A feedstock, that normally comes in the form of a powder or wire, a heat source that can be a laser beam, an electron beam or a high-energy electric arc and a motion system. When these components are combined together, the consolidation or deposition of individually shaped layers can be fused together to obtain a 3D solid following a layer-by-layer approach.

Despite the clear advantages of AM, many challenges must be addressed before these processes can be qualified for the manufacturing of critical application components. Some of the main factors during manufacturing that are critical to ensure the satisfactory performance of AM components are summarized in **Figure 1-1.**

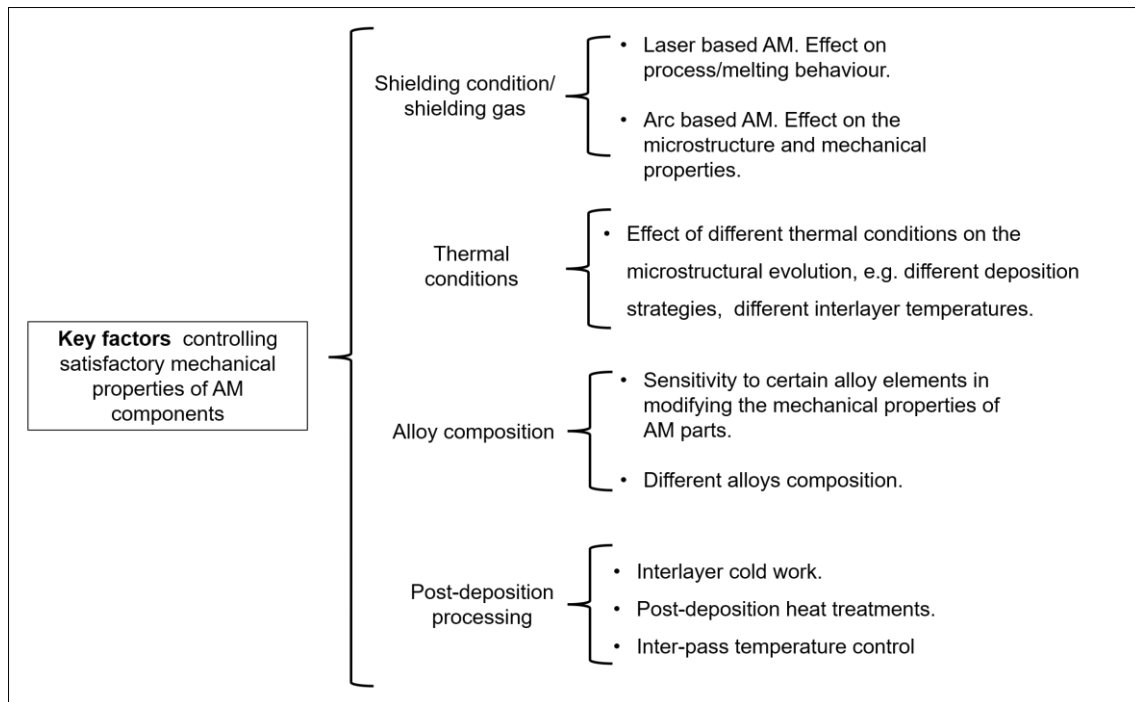


Figure 1-1. Key factors affecting the mechanical properties during AM processes.

Even though these factors form part of every AM technology, it is expected that some of them will have different degrees of criticality depending on the heat source and feedstock used. For example, for the powder-based AM, one of the most extensively used processes is the laser powder bed fusion (L-PBF) technology. Due to the laser-powder interactions phenomena, the L-PBF is a highly dynamic process which leads to unstable melting behaviour. Hence, one of the main challenges of this process is to minimize defects such as pores and lack of fusion that can be detrimental to the mechanical properties. Nevertheless, L-PBF is also a low heat input process, this contributes to the development of microstructural features that provide good mechanical performance. This makes it apparent that, for a process such as L-PBF, more focus must be dedicated to the process factors that can have an important effect on the melting stability, such as shielding gas or powder melting parameters.

For the wire-based AM, the Wire and Arc Additive Manufacturing (WAAM) has been the main area of research at the Welding and Additive Manufacturing Centre (WAMC) of Cranfield University for the past 12 years. In contrast to the previously described L-PBF process, the WAAM technology has no stability issues

regarding the melting behaviour. Hence, defects such as pores and lack of fusion are generally not the main concern and fully dense components can be obtained. However, the high energy arc used in WAAM and the larger thermal fields as compared to L-PBF, make this a high heat input process which can induce multiple solid-state transformations during the various heating and cooling cycles which make the control of the microstructure one of the main challenges of this technology.

It is clear that the L-PBF and WAAM processes represent two extremes in terms of process stability and heat input. Hence, they are perfect candidates to investigate the criticality of different factors of the AM processes depending on each of the process's key features. For L-PBF, the main requirement to obtain satisfactory mechanical properties is to ensure process melting stability to avoid defects, while the WAAM process requires careful control of the final microstructure developed to ensure good mechanical performance. Therefore, it is hypothesised in this work that mechanical properties can be improved in L-PBF by improving the melting stability of the process and that the mechanical performance of WAAM components can be ensured by focusing on the right microstructure that can be obtained through the management of the thermal profiles, thermal behaviour and post-deposition treatments of the alloys in question. In order to investigate how critical, the various factors presented in **Figure 1-1** are on the mechanical properties of L-PBF and WAAM components, the specific research approach shown in **Figure 1-2** was followed in this work.

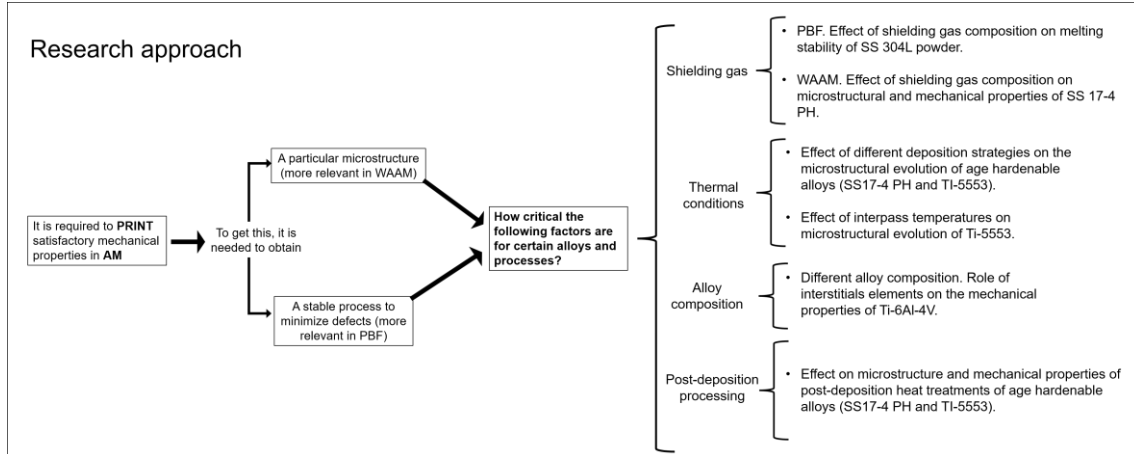


Figure 1-2. Research approach followed to investigate the criticality of various factors on the mechanical properties of various alloys and AM processes.

Regarding the PBF process, it is studied how the shielding gas composition affects the melting stability and bead geometry during selective laser melting (SLM) of SS304L powder. This alloy is a well-known L-PBF material, hence it was considered as a good candidate to investigate this correlation. For the WAAM process, where achieving the right microstructure is paramount, it becomes particularly interesting to investigate the effect of different thermal conditions on the microstructural evolution of age hardenable alloys. This is because the complex combination of multiple heating and cooling cycles during WAAM is expected to modify the morphology and distribution of the various precipitates which will correlate with different mechanical performances. Two age-hardenable alloy systems are proposed as part of this work to study the aforementioned correlation, stainless steel 17-4PH and near- β titanium alloy Ti-5553. The former is normally used in corrosive environments where superior strength and corrosion resistance are demanded, while the latter finds its application in aerospace components where high strength-to-weight ratios are required such as landing gears.

Ti-6Al-4V is the workhorse of the titanium alloys used in the aerospace industry. For this reason, its behaviour and mechanical properties during WAAM have been heavily investigated during the past decade. However, since titanium is highly reactive to oxidation, factors such as the sensitivity to embrittlement due to oxygen incorporation during WAAM processing have not been clearly defined.

Hence, the role of oxygen in the WAAM of Ti-6Al-4V has also been considered as part of this work in order to identify the oxygen concentration limits as an interstitial element that can be detrimental to the mechanical properties.

Thanks to the inherent flexibility of AM processes it is also possible to apply additional methods to improve the mechanical properties. This can be in the form of post-deposition heat treatments or interlayer mechanical work. As an effort to investigate how the mechanical properties of the age hardenable alloys considered in this work, SS 17-4 PH and Ti-5553, can be furtherly improved, the effect of post-deposition heat treatments has also been considered. In specific, the influence on mechanical properties of standardised post-deposition ageing heat treatments on SS 17-4PH and Ti-5553 is to be studied.

1.2 Aim and objectives.

The aim of this PhD research is to investigate the criticality of certain process parameters of various AM technologies in terms of stability and mechanical properties in order to optimise the process and improve mechanical performance. This correlation between processing conditions and mechanical properties of the alloys and processes considered in this work still needs to be elucidated.

The objectives are listed below:

1. To study the effect of different shielding conditions on melting behaviour, microstructure and, mechanical properties during L-PBF of SS304L and WAAM of age hardenable alloy 17-4 PH. (Chapters 4 and 5).
2. To investigate the microstructural evolution during WAAM of age hardenable alloys 17-4PH and Ti-5553 and the role of different thermal cycles on the developed microconstituents and mechanical properties. (Chapter 5)
3. To investigate the effectiveness of post-deposition heat treatment of WAAM 17-4PH and Ti-5553 as a way to improve the mechanical properties obtained. (Chapters 5 and 6).
4. To understand the effect of different oxygen contents on the embrittlement of WAAM Ti-6Al-4V and to identify tolerance levels for oxygen concentrations. (Chapter 7).

1.3 Thesis structure.

The thesis is structured in paper format as outlined by Cranfield University on the thesis format guidance document (Guidance Document: Format options for PhD Thesis V1.3 January 2017). The thesis consists of a total of eight chapters. Chapters 1 and 2 contain the introduction and methodology, respectively. A literature review chapter is not required for a paper-format thesis, according to the aforementioned guidance document. However, in order to make the thesis more readable, Chapter 3 presents a literature review to contextualize the research approach of the thesis and to introduce the reader to relevant metallurgical aspects of the alloys of concern and their behaviour during traditional welding processes and other existing AM technologies. Chapters 4 to 7 are the main technical chapters containing the main outcomes of the PhD thesis. Finally, Chapter 8 contains the implications of the work, key findings and future work recommendations. A brief description of each chapter is presented below:

Chapter 1. This chapter introduces the research background, research gap, aim and objectives, and the thesis structure.

Chapter 2. This chapter presents the principal research methodology implemented to carry out the entire PhD research, including the bespoke methods and equipment developed especially for this work.

Chapter 3. The chapter contains a supplementary literature review covering the role of the shielding atmosphere on laser processing and the relevant physical metallurgy aspects of the alloys of concern.

Chapter 4. This chapter presents the study of the effect of shielding conditions on the melting behaviour and process control during L-PBF AM of SS304L powder.

Chapter 5. This chapter presents the work done on WAAM of 17-4 PH. Including the effect of different shielding conditions on microstructure development and including the effect of different thermal cycles and post-deposition heat treatments on the mechanical properties.

Chapter 6. This chapter presents the work performed on the WAAM of Ti-5553. Including the microstructure and mechanical properties obtained in response to different inherent thermal cycles and the effectiveness of post-deposition heat treatments to improve mechanical properties.

Chapter 7. This chapter presents the systematic study of oxygen content in Ti-6Al-4V WAAM and its role in the mechanical properties and embrittlement of this alloy.

Chapter 8. This chapter presents the overall discussion, contribution to knowledge, and future work.

1.4 Publication contributions.

Three research papers were published during the completion of this Phd. Below it is summarised the credits of each publication together with the author's contribution.

Chapter4.

A. Caballero, W. Suder, X. Chen, G. Pardal , S. Williams. *Effect of shielding conditions on bead profile and melting behaviour in laser powder bed fusion additive manufacturing*. Additive manufacturing 34 (2020) 101342. doi: <https://doi.org/10.1016/j.addma.2020.101342>.

A. Caballero (80%): conceived and design the analysis. Experiments execution. Collected the data. Contributed data or analysis tools. Performed the analysis. Wrote the paper.

W. Suder (10%): conceived and design the analysis. Paper review.

X. Chen (2.5%): Contributed data or analysis tools

G. Pardal (2.5%): Contributed data or analysis tools

S. Williams (5%): conceived and design the analysis. Paper review.

Chapter 5.

A. Caballero, J. Ding, S. Ganguly, S. Williams. *Wire + Arc Additive Manufacture of 17-4 PH stainless steel: Effect of different processing conditions on microstructure, hardness, and tensile strength*. Journal of Materials Processing Technology. 268 (2019) 54-62. doi: <https://doi.org/10.1016/j.jmatprotec.2019.01.007>.

A. Caballero (85%): conceived and design the analysis. Experiments execution. Collected the data. Contributed data or analysis tools. Performed the analysis. Wrote the paper.

J. Ding (10%): conceived and design the analysis. Paper review.

S. Ganguly (2.5%): Contributed data or analysis tools. Paper review.

S. Williams (2.5%): Paper review.

Chapter 6

A. Caballero, A.E. Davis, Kennedy J.R, J. Fellowes, A. Garner A, S. Williams, P. Prangnell. *Microstructural characterisation and mechanical properties of Ti-5Al-5V-5Mo-3Cr built by wire and arc additive manufacture*. Philosophical Magazine. (2022). doi: <https://doi.org/10.1080/14786435.2022.2113470>.

A. Caballero (75%): conceived and design the analysis. Experiments execution. Collected the data. Contributed data or analysis tools. Performed the analysis. Wrote the paper.

A.E. Davis (10%): conceived and design the analysis. Contributed data or analysis tools. Performed the analysis. Review the paper.

J.R Kennedy (5%): Contributed data or analysis tools. Review the paper.

J. Fellowes (1%): Contributed data or analysis tools.

A. Garner (1%): Contributed data or analysis tools.

S. Williams (4%): conceived and design the analysis

P. Prangnell (4%): Review the paper.

2 Methodology.

2.1 Literature review.

The literature review of this work covers the influence of shielding gas composition on melting behaviour during laser welding and laser-based additive manufacturing. It also includes the effect of shielding gas in the microstructural features of 17-4 PH during AM processing under different technologies and the metallurgical properties of 17-4PH and Ti-5553, both age-hardenable alloys. The response to in-process thermal cycling and heat treatments has also been included. Finally, the role of interstitial elements on Ti-6Al-4V has been included and its effect on the mechanical performance has been investigated, both during the traditional processing of this alloy and also during AM processes. The following procedure was implemented to carry out the literature review.

1. Formulating research question: research gaps were identified from both project requirements and the preliminary revised literature on each topic.
2. Identifying keywords: the following keywords were used for the preliminary literature search: additive manufacturing, powder bed fusion, WAAM, shielding gas, 17-4 PH, Ti-5553, heat treatment, microstructural evolution, Ti-6Al-4V interstitials.
3. Search the extant literature: covered the most representative works of published data in the given field. This included the search of books, conference papers, MSc and PhD theses and research papers. This search was based entirely online, and databases and search engines such as Scopus, Springer, Science Direct and Google Scholar were used.
4. Paper screening: the found papers passed a screening process where only the abstract and conclusions sections were read and their relevance to the research question was established. Irrelevant publications were discarded, and the relevant ones were archived and organised using Mendeley.
5. Paper analysis: the most relevant papers were analysed throughout, and the findings were used to establish the research gap and research route for each of the work packages. This was the source of information used

for the introduction and discussion sections of each chapter and for the extended literature review chapter (Chapter 3).

2.2 Research focus identification.

The present PhD thesis was completed as a part-time degree and various work packages were initially determined by the requirements of existing industrial and EPSRC projects at the WAMC. However, the revised literature allowed to identify further research gaps and helped in designing additional experiments, analysis, and tests in each case to make sure that rigorous research of enough quality to award a PhD degree of relevant contribution to knowledge was completed. Based on these, the research focus can be broken down into the following topics:

1. Effect of shielding gas composition on the melting behaviour during laser-powder bed fusion AM. At the time when the study was planned, no detailed research has been carried out in studying the effect of different shielding gas compositions on the melting stability of fibre lasers used during powder bed AM. Additionally, the effect of shielding gas composition on bead profile geometry remained also unexplored.
2. 17-4 PH and Ti-5553. Both of these alloys are expected to have a complex response to the repetitive heating and cooling cycles inherent to AM as they are age-hardenable alloys. The effect of laser and powder processes on microstructural evolution is well established in the literature. However, the effect of arc heating sources such as the ones used in WAAM, which translate in very dissimilar thermal conditions, has not been studied. The effectiveness of “standard” heat treatment for these alloys after arc-based deposition also remained unexplored.
3. Ti-6Al-4V and the role of interstitial during WAAM. The role of oxygen and other interstitial elements on the embrittlement of Ti-6Al-4V has been investigated before for traditional manufacturing routes such as casting and forging. However, the concentration limits allowed during AM have not been clearly identified and the tolerance of the microstructural features developed during WAAM to embrittlement due to interstitials pick up during the process has not been systematically investigated before.

2.3 Experimental work and bespoke developments.

The entire experimental work for the manufacturing of the samples was carried out in the WAMC by the author. For the work in Chapter 4, an in-house specially developed powder bed testing rig was assembled. The author of this thesis was responsible for this setup to work properly and various iterations of hardware modifications and optimisations were necessary in order for the equipment to perform the trials satisfactorily. Work in Chapters 5, 6 and 7 was completed using the WAAM cells available at the WAMC, which counts with a wide variety of welding power sources (MIG-CMT and Plasma transferred arc in this case), different motion systems (6-axis industrial robots and CNC machines) and various ways of providing an inert gas shielding atmosphere (local and global shielding). The thermal data required for Chapter 6 was recorded using a thermocouple harpoon device that enabled the insertion of an R-type thermocouple into the melt pool and continue the recording of the thermal cycles in real time as more layers were added. This device was entirely designed from scratch by the author and it proved to be successful in measuring the thermal cycles during the WAAM deposition process. This was key in establishing a quantitative correlation between the microstructural evolution of Ti-5553 and the thermal history. This device is now available at the WAMC to be used in other projects.

Microstructural characterization of the samples produced was performed by means of optical microscopy, scanning electron microscopy, and electron backscattered diffraction. All the characterization tests were performed at Cranfield University by the author with the exception of the EPMA and EBSD maps presented in Chapter 6. The EPMA maps were done at Manchester University as Cranfield does not count with such equipment. The EBSD maps for this chapter were also performed at Manchester as the detector was not working at Cranfield at the time. All the mechanical tensile testing was also performed by the author at the Mechanical testing laboratory at Cranfield. The only exception was some of the tensile data presented in Chapter 6 which was obtained by an external testing house as Cranfield University facilities were not available at that time.

Standard quality procedures for welding processes were applied in the manufacturing of the WAAM samples to ensure sound joints. This included but was not limited to: proper substrate and feedstock preparation and ensuring adequate shielding conditions during deposition. Where required, the microstructural analysis was performed through standardised stereological techniques to provide unbiased quantitative characterization. An adequate sample size was considered to achieve representative results. All mechanical testing was performed following the relevant standardised procedures.

3 Extended literature review.

Every individual technical chapter (Chapters 4 to 7) has its own specific literature review included in the introduction section. However, the present chapter serves as an extended literature review providing the required pre-knowledge to better understand the scope of the thesis.

3.1 Effect of shielding conditions on laser melting behaviour of materials.

3.1.1 Introduction. Variables involved in laser processing of materials.

Laser welding is generally characterized by high energy densities and reduced heat input, which represents some of its main advantages. Additionally, the concentrated beam of monochromatic laser light can be positioned accurately into a small spot that allows precise control over the weld position and heat-affected regions, which usually offer good control over the microstructural features developed [1,2]. These characteristics make laser welding an attractive technology to join a wide variety of alloys. The main process variables for a given material and laser systems are, beam power, focused spot size and welding speed [3]. Depending on the power used, laser welding can be classified into two modes, conduction and keyhole welding. Each of these melting regimes is controlled by a different mechanism and can produce very different melting characteristics and weld profiles [2].

Conduction laser welding corresponds to the regime when relatively low laser power densities are used. In this type of welding, the heat provided by the beam energy is transferred into the material by conduction. Hence, a hemispherical weld bead is formed similar to the one obtained in conventional fusion welding processes [2]. Conduction welds normally have aspect ratios of around 1 and no material vaporization occurs. On the other hand, keyhole welding takes place when the energy density applied is high enough to produce metal vaporisation, this increases the local vapour pressure that drills a depression in the melted metal forming a deep and narrow cavity that remains open due to the balance

between the surface tension and recoil pressure. Keyholes can reach depth-to-width ratios of up to 100 and allow to effectively weld thick sections of material at relatively fast speeds [3]. Regardless of the welding mode utilise, controlling the geometry of the laser weld process is paramount to ensure that the quality and geometric requirements of the joint are met.

During keyhole welding, part of the laser beam energy is absorbed by the metal vapour inside the weld which increases the kinetic energy of the beam photons, ionizing the metal vapour and creating a high temperature plume plasma gas, both inside the keyhole and also on its surface [2]. The inner plasma is effective in coupling the laser beam to the workpiece improving the energy transferred to the welded joint [4]. Conversely, the external plasma at the surface can reflect and defocus the laser beam, lowering the overall efficiency of the process by gradually weakening the laser intensity [5]. This can create process instabilities and disruptions during the laser welding process. Due to these laser beam-plasma plume interactions, the shielding gas composition has also been identified to be a key parameter for laser welding processing [6–8].

3.1.2 Effect of shielding gas composition on melting stability and bead profile during laser welding. Commonly used gases used during laser welding and problems.

Due to the criticality of the shielding conditions on the melting behaviour during laser welding, various investigations have covered the effect of shielding gas composition, on the bead geometry obtained, e.g. weld penetration, and melting stability of the laser process. It has been established in the literature that the shielding gas chemistry has a more significant effect when CO₂ lasers are used as opposed to fibre lasers. This is a consequence of the interaction between the laser beam and the plasma plume at different wavelengths.

It has been determined that an increase in the inverse Bremsstrahlung absorption coefficient, which reflects the amount of laser energy that is absorbed by the plasma plume, is proportional to λ^2 , where λ is the laser wavelength [9]. CO₂ lasers have a wavelength of 10.64 μm while fibre lasers such as Nd:YAG lasers have a wavelength equal to 1.064 μm , this makes the CO₂ laser sources more

prone to laser-plasma plume interaction issues. **Figure 3-1** shows the measured refractive index and Inverse Bremsstrahlung coefficient of the plasma plume for different plasma temperatures for the two types of aforementioned laser sources. It is clearly shown that the refractive index is equal to 1 for Nd:YAG lasers for any given temperature, which is equivalent to the index for a vacuum atmosphere where no laser light bending capabilities exist. Hence, no significant disruption of the incident laser beam by the plasma plume would be expected. For the Inverse Bremsstrahlung coefficient, the values increase significantly in CO₂ laser as compared to Nd:YAG for the same plasma temperature (**Figure 3-1b**) [10]. This means that a higher percentage of the laser energy will be absorbed by the plasma plume, disrupting the melting stability of the workpiece and the bead profile obtained.

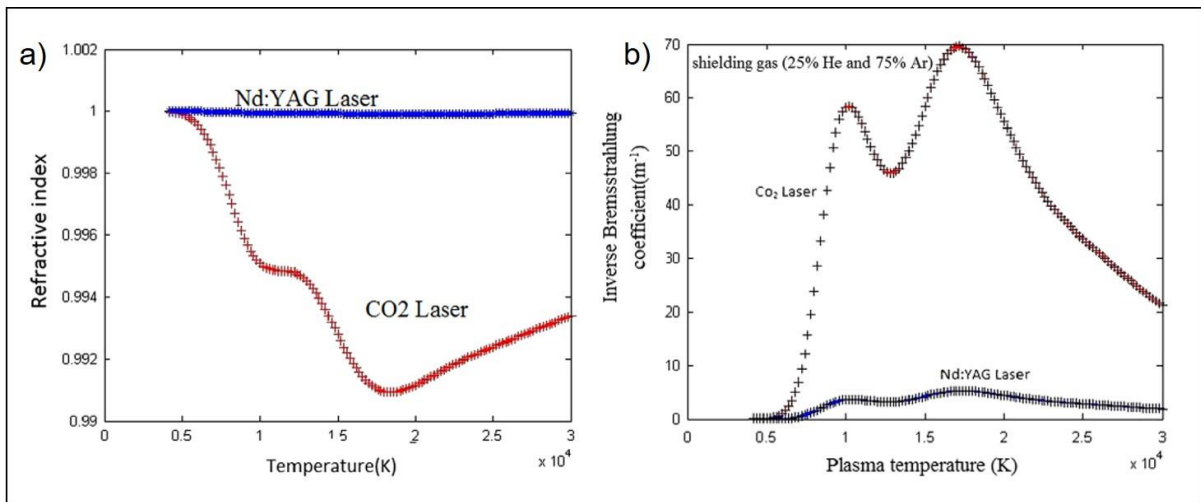


Figure 3-1. a) refractive index coefficient as a function of temperature for CO₂ and Nd:YAG lasers; b) inverse Bremsstrahlung absorption coefficient as a function of plasma temperature for CO₂ and Nd:YAG lasers [10] .

Various investigations have carefully measured to what extent the shielding gas composition affects the bead profile during welding with CO₂ lasers. As previously explained, plasma plume energy absorption for this type of laser is significant, causing the laser energy that reaches the substrate to be reduced which manifests as a decrease in penetration. Hence, it is paramount to control and suppress the plasma plume formation in the first place as much as possible. In a study that covered the influence of various shielding gas compositions on the

weldability of steel, it was found that Helium, and 50% Argon + 50% Nitrogen mix provided the highest penetration and formability among the other gases used, which also included pure argon, carbon dioxide and 100% nitrogen. These findings were believed to be closely related to the higher ionization potential of the successful mixes that enabled the most efficient minimization of the plasma plume formation and thus, its interaction with the incident laser beam. Dissociation potential, thermal conductivity and the atomic weight of the shielding gases were also found to have an influence on the melting characteristics [11]. These findings agree with similar other research in the field of CO₂ lasers under different shielding conditions. For example, it has been found that in hybrid welding using laser and arc-based welding, helium suppresses the formation of laser-induced plasma when a minimum of 30%-40% helium on the shielding gas mix is added [12]. Similarly, another study on hybrid welding identified an optimum content of 50% for increased penetration and it was concluded that laser-induced plasma plume generation is in inverse proportion to penetration depth [13]. It is due to these findings that it has been established, as a common industrial practice, to incorporate some content of helium in the shielding gas during CO₂ laser welding [14].

For fibre lasers, it is commonly assumed that shielding gas has no or little effect on the melting behaviour and process stability during fibre laser welding. Hence, argon is normally used as the standard gas [15]. However, some studies seem to suggest otherwise. For example, it has been shown that for the welding of aluminium alloys, both argon and helium can be used effectively to produce quality welds. Even though both processes are stable with each of the gases, it was found that differences in the bead profile do exist between each of the gases. In this case, helium resulted in an excessive weld width due to higher thermal conductivity as compared to argon and produced an overall better weld quality [16]. The amount of porosity in the weld, which can be a consequence of the degree of melting instability, has also been shown to be strongly dependent on the shielding gas composition used, with additions of oxygen and CO₂ minimising pores formation [17–19]. This evidence suggests that it is still important to

carefully consider what gas composition is to be used for the shielding gas during fibre laser welding in order to produce good quality welds.

The effectivity of argon as a suitable shielding atmosphere for fibre welding has been attributed to its capability of blowing away the plasma plume efficiently due to its higher density as compared to helium. It is for this reason that it has been observed that using argon during fibre welding increases penetration depth as compared to using pure helium and, as more helium is added to the mix, the penetration starts to decrease [20]. However, this effect has only been evaluated under the condition that a constant stream of gas is applied directly on top of the welding pass. For powder-based additive manufacturing processes, this effect cannot be exploited to the same extent as the shielding gas flow cannot be applied directly into the powder bed-laser beam interaction point as the powder particles would be blown away. Hence, the effectiveness of argon gas as the shielding gas of choice for laser and powder additive processes still needs further elucidation. Nevertheless, it is because of the previous experience based on fibre laser welding that argon has been the standard shielding gas used during L-PBF AM.

3.1.3 Effect of shielding gas composition on melting behaviour during laser powder bed additive manufacturing.

The most recent generation of fibre lasers represented several advantages as compared to other laser sources that were particularly beneficial for powder-based additive manufacturing machines. Firstly, fibre lasers can deliver high energy efficiency together with good beam quality at a small beam focus diameter, which is ideal for the melting of fine powder particles. Additionally, fibre lasers are relatively compact and robust making their installation in L-PBF systems advantageous from the engineering point of view. For these reasons, fibre lasers became the type of lasers used for commercial L-PBF AM setups. The shielding gas normally used for this process is argon gas which has been taken from previous experience in fibre laser welding, as mentioned in the previous section. Henceforth, only a limited number of studies have been dedicated to investigating the role of the shielding gas composition on the melting

characteristics and bead profile of L-PBF AM and more efforts have been focused on evaluating the role of different gas flow rates of argon instead. The nature of the shielding gas flow is important to remove the process by-products and minimize the laser attenuation by the plasma plume. The studies agree and conclude that increasing the cross-gas flow rate above 2 m/s ensures higher bead penetration, more stable melting, and lower levels of porosity [21–23].

Regarding the effect of the shielding gas composition on bead geometry, it has been shown that for the L-PBF of Inconel powder, using argon or helium leads to similar penetration depth. However, different shielding gas compositions did influence the main phenomena surrounding the melt pool, such as spatter generation and denudation zone width [24]. On the other hand, another work that also experimented with using different shielding gas compositions reported that using argon gas has a stabilising effect on the melt pool while using a mix of helium and nitrogen produces fluctuations in the penetration depth, showing that different shielding gas can affect the bead shape as well [25].

Shielding gas composition have also been shown to determine the final mechanical properties of the deposit. For example, previous publications have stated that it is possible to promote the in-situ modification of the microstructures and properties of laser PBF consolidated material by supplying the suitable reactive gas locally in the region of the laser-powder interaction [26]. Using argon or nitrogen to perform laser PBF of aluminium alloys produces components of higher ductility as compared to the counterpart built using helium, showing once again that the chemical composition of the shielding gas atmosphere is an important parameter to consider when it comes to determining mechanical properties [27]. Additionally, it has also been shown that the partial pressure of the shielding atmosphere also influences the melting behaviour and bead profile obtained. This has been investigated by performing laser PBF under low and high-pressure atmospheres. For low-pressure atmospheres, it was found that excessive denudation reduces the bead profiles since the particles are repelled by the plume [28]. On the other hand, using helium can increase penetration

depth under high-pressure atmosphere inside the printing chamber thanks to the reduced formation of spatter and plasma under this gas [29].

3.2 Stainless steel 17-4PH

3.2.1 Introduction. Alloy classification, composition, and applications.

Stainless steel 17-4 PH (15-17.5%Cr, 3-5%Ni, 3-5%Cu, 1%Mn, 1%Si %wt) is a precipitation-hardened martensitic grade that offers high strength and good corrosion resistance in aqueous environments. The high strength of this alloy comes from the precipitation of fine coherent copper particles in a martensitic matrix during the ageing step [30]. This alloy is normally used as a structural material for chemical and power plants, aircraft fittings, fasteners, pump shafts, gears, paper mill equipment and jet engine parts [31,32].

3.2.2 Production of 17-4PH. Common manufacturing route. Microstructure and mechanical properties of the wrought alloy.

For most 17-4PH components, the manufacturing steps include the casting of the billet, followed by the forging steps and the final heat treatment. These steps are summarized in **Figure 3-2**. Forging normally takes place around 1200 °C and the solutionizing step at 1040 °C. The ageing temperature and time depend on the target properties.

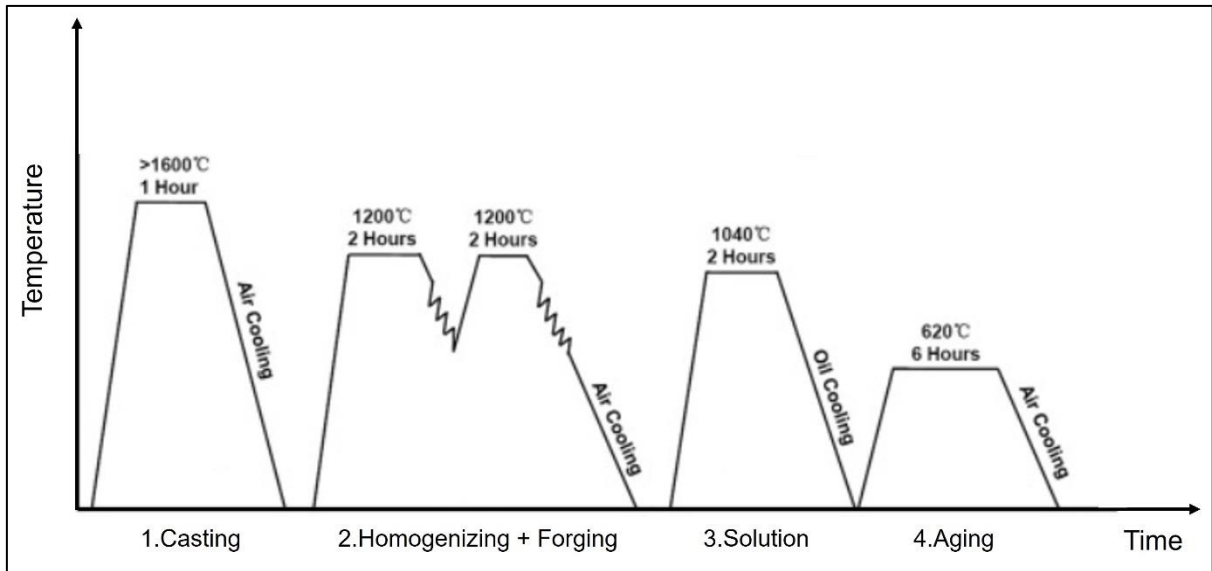


Figure 3-2. Schematic showing the processing steps of 17-4 PH forged components. Modified from [33].

The typical microstructure obtained after forging and ageing of 17-4 PH is presented in **Figure 3-3**. This is formed mainly by aged lath martensite with some small percentages of δ -ferrite and retained austenite.

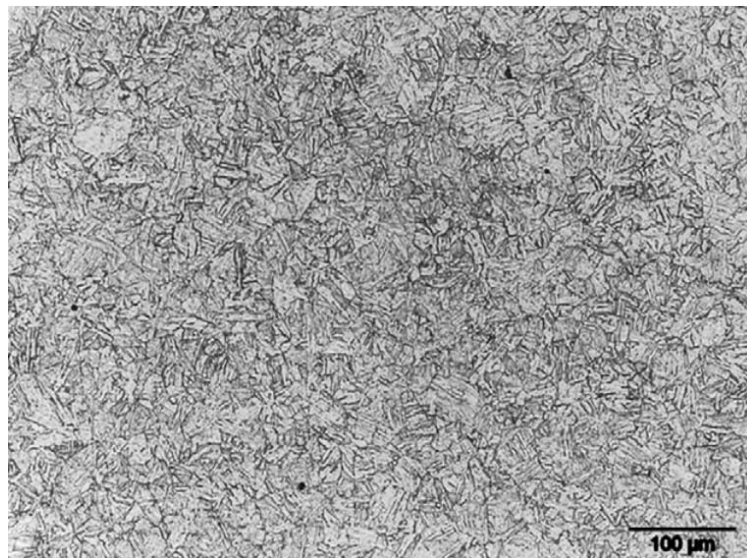


Figure 3-3. Typical microstructure of forged and aged 17-4 PH [34].

On the forged and aged condition, volume fractions of retained austenite tend to be low and can only be detected by using techniques such as EBSD or X-ray

diffraction. **Figure 3-4** shows an example of the retained austenite found at the prior austenite grain boundaries identified through EBSD showing the small volume fraction that this phase represents with respect to the martensitic matrix. In the peak-aged condition, such microstructural features give a tensile strength of approximately 1379 MPa with elongation values of approximately 14% [35]. More details on the different heat treatment routes will be given in a later section of this chapter.

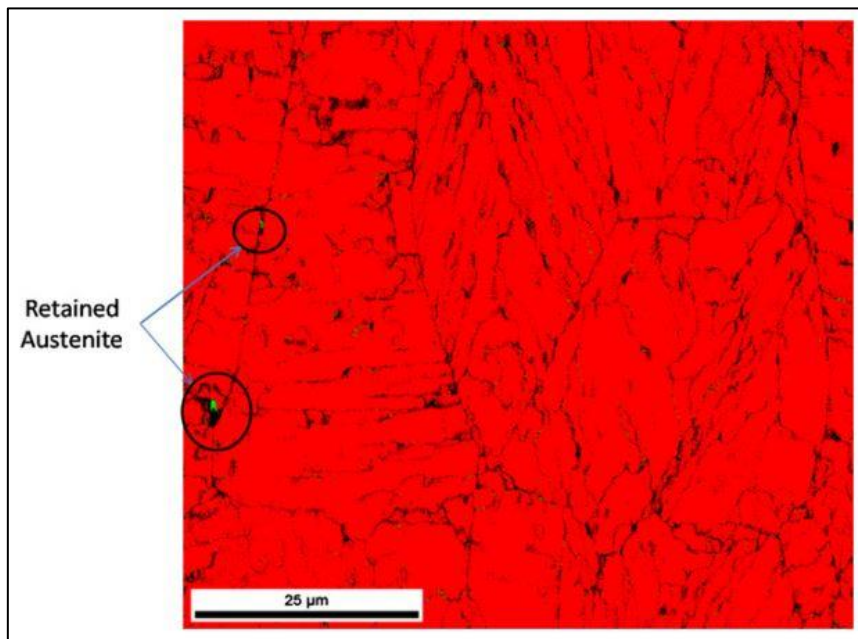


Figure 3-4. EBSD phase map for an annealed 17-4 PH showing the retained austenite (green) within the martensitic matrix (red) [35].

3.2.3 Physical Metallurgy. Equilibrium and non-equilibrium phase transformations upon cooling.

To understand the phases that develop during the processing of 17-4 PH, the phase diagram is presented in **Figure 3-5**. As can be seen, upon solidification from the liquid, the first phase to form is δ -ferrite. Continuation of the cooling derives into liquid, δ -ferrite and γ -austenite coexisting together. Once all the remaining liquid has been consumed, the constituent phases are δ -ferrite and γ -austenite. Further cooling produces mainly only γ -austenite. However, this solidification sequence at the high temperature range applies only for equilibrium

cooling conditions where the times are long enough to allow complete diffusion of the chemical species.

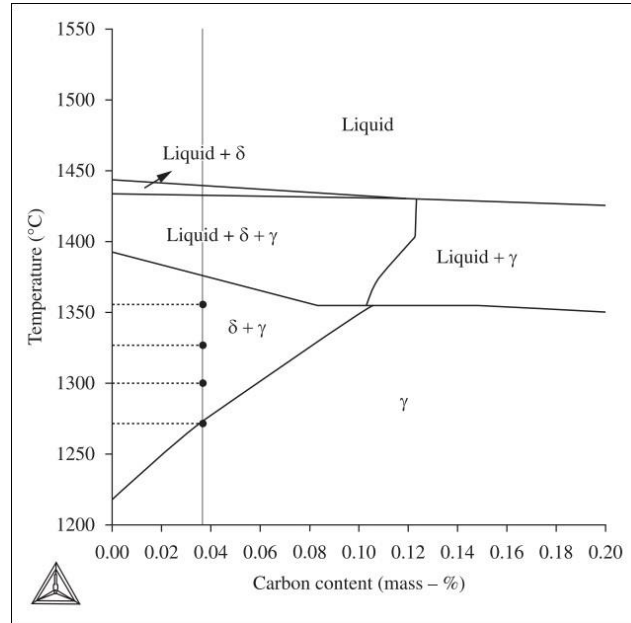


Figure 3-5. Phase diagram of 17-4 PH alloy [36].

To determine what type of microstructure is developed in industrial processes such as forging, welding and additive manufacturing, it is useful to consider the Schäffler diagram (**Figure 3-6**). This diagram was developed for stainless steels under the rapid cooling conditions of welding processes. To determine where the alloy 17-4 PH stands on this diagram, it is necessary to calculate the chromium equivalent (Cr_{equ}) and nickel equivalent (Ni_{equ}) which represent the weighted sum of the elements that promote the formation of δ -ferrite and γ -austenite respectively. These values are calculated from **Equations 3-1** and **3-2** [37].

$$Cr_{equ} = Cr\% + 1.5 \cdot Si\% + Mo\% + 2.0 \cdot Ti\% + 0.5 \cdot Nb\% \quad (3-1)$$

$$Ni_{equ} = Ni\% + 0.5 \cdot Mn\% + 30 \cdot C\% \quad (3-2)$$

For 17-4 PH stainless steel the Cr_{equ} is equal to 19.7 while Ni_{equ} is equal to 7.6. This point has been indicated in **Figure 3-6** by the black circle. From this diagram, it can be estimated that after a process such as welding or AM, this alloy will contain between 20% and 40% of δ -ferrite and the rest will be formed by γ -

austenite and martensite. The percentage of each phase will be determined by the processing conditions.

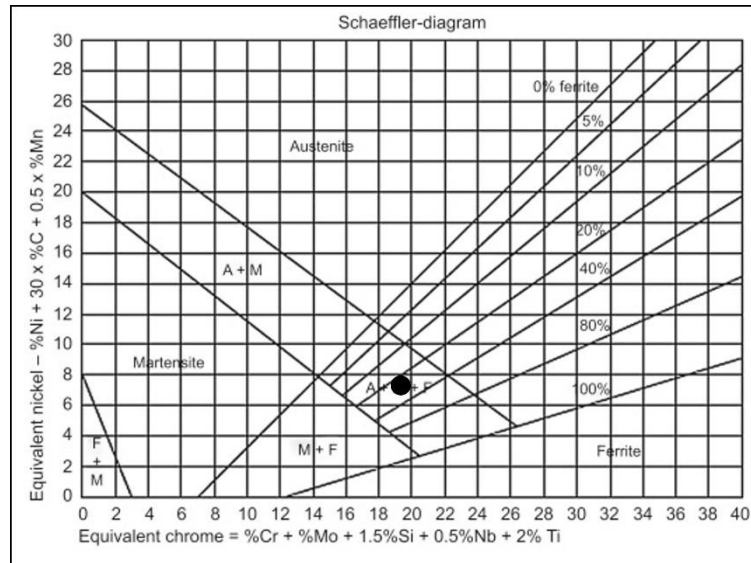


Figure 3-6. Schaeffler diagram to determine the possible phases of 17-4 PH alloy (black circle). Adapted from [37].

The presence of retained γ -austenite at room temperature depends on the actual application of the alloy and can be either beneficial or detrimental. However, for most applications where high strengths are required, it is desirable to limit the formation of retained γ -austenite as much as possible as this phase cannot be age hardened by the copper precipitates due to their higher solubility in the austenitic phase [38]. The amount of retained γ -austenite depends on the chemical composition, cooling rates and austenitic grain size. If the amount of γ -austenite stabilizing element or cooling rates are too high, then the austenite will not completely decompose into martensite and will become metastable at room temperature [39]. The austenitic grain size plays a role in the austenite retention through a mechanical stabilization mechanism that restricts the volumetric change associated with the austenite to martensite phase transformation. This mechanism will be described in further detail in Chapter 5 of this work. The retained γ -austenite is a metastable phase in 17-4 PH, and it can be transformed into martensite by applying cold work, which is a martensitic stress-induced transformation, or by exposure at extreme subzero temperatures, below the martensite finish temperature M_f [40]. It is for the aforementioned reasons, that

the control and reduction of the percentages of retained γ -austenite in the final product is one of the major points of focus when welding and additive manufacturing procedures are developed for this alloy.

3.2.4 Heat treatment: precipitation kinetics, heat treating procedure, precipitation reactions.

To achieve the maximum levels of strength for 17-4 PH, a heat treatment must be applied. The common heat treatment procedures are summarised in **Table 3-1**, and it includes an austenitizing stage followed by ageing.

Table 3-1. Heat treatment specifications for 17-4 PH. Modified from [41].

Condition	Solution heat treatment temperature	Aging treatment temperature	Time at temperature	Type of cooling
A	1038 °C (1900 °F)	NA	15-20 min	Air
H900	1038 °C (1900 °F)	482 °C (900 °F)	1 hour	Air
H925	1038 °C (1900 °F)	496 °C (925 °F)	4 hours	Air
H1025	1038 °C (1900 °F)	551 °C (1025 °F)	4 hours	Air
H1075	1038 °C (1900 °F)	580 °C (1075 °F)	4 hours	Air
H1150	1038 °C (1900 °F)	621 °C (1150 °F)	4 hours	Air

The austenitizing temperature is the same for any of the ageing routes and it must be performed at 1038 °C for 15 to 30 minutes depending on the component

geometry and thickness. A material in this condition is referred to as “Condition A”. For the subsequent ageing treatment, various options are available, and they are designated by the letter “H” followed by a number that represents the ageing temperature in degrees Fahrenheit. The H900 ageing treatment is referred to as the “peak ageing condition” as it gives the highest value of strength. For the other treatments, the ageing temperature increases while the mechanical strength decreases and the elongation increases. The approximate tensile mechanical properties and hardness that are expected for each heat treatment condition are summarised in **Table 3-2**.

Table 3-2. Approximate mechanical properties for each heat treatment condition of 17 4-PH [42].

Property	H900	H925	H1025	H1075	H1100	H1150
UTS (MPa)	1379	1310	1172	1138	1034	1000
0.2% YS (MPa)	1276	1207	1138	1034	931	862
Elongation %	14	14	15	16	17	19
Brinell Hardness	420	409	352	341	332	311

3.2.5 Welding of 17-4PH. Procedures and issues.

The weldability of 17-4 PH is normally regarded as good, and it is similar to that of austenitic stainless steel. Common arc welding procedures for 17-4 PH have been applied successfully including tungsten inert gas (TIG) and plasma transferred arc welding (PTA) [43]. Normally, welding of 17-4 PH does not require a preheating step for sections up to 100mm. However, the ductility of the weld metal can be rather low which increases the likelihood of cracking. Hence, for some applications, welding is performed on Condition A or in the overaged state in order to ensure a softer base material that can accommodate the residual

stresses better. An alternative approach has been to use a softer material for the filler metal, such as an austenitic stainless case, for applications where lower strength of the joint can be allowed [44]. The typical microstructure of the weld metal is shown in **Figure 3-7** and is mainly formed by δ -ferrite in a martensitic matrix. The contrast between the as-forged microstructure presented in **Figure 3-3** and the weld metal is evident. The larger volume fraction of δ -ferrite in the weld metal as compared to the forged counterpart will give lower tensile strength values together with lower ductility as the δ -ferrite-martensite interfaces serve as stress concentrators for cracking due to their different response to the applied strain.

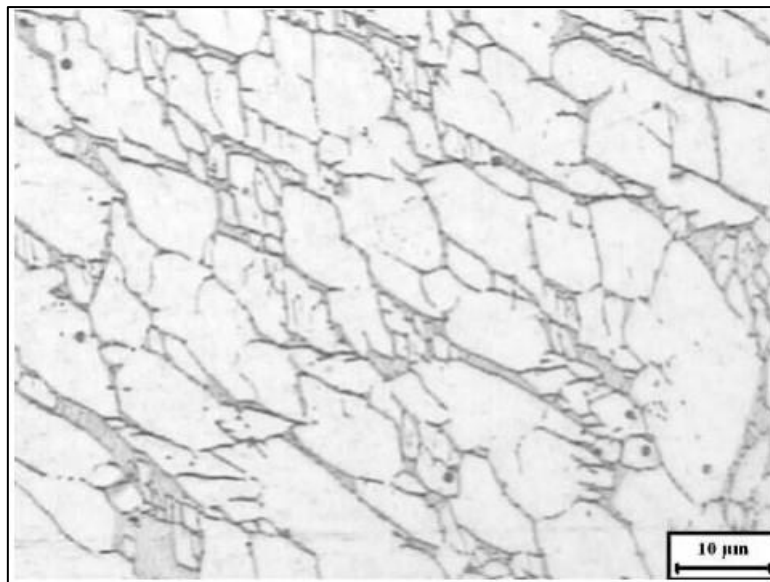


Figure 3-7. Typical microstructure of 17-4 PH weld metal using TIG [44].

With regards to the heat-affected zone (HAZ), it has been clearly identified that softening of the base plate takes place in the adjacencies of the weld. As can be seen in **Figure 3-8**, the hardness drops as compared to the base plate when welding is performed on a plate in Condition A and also heat treated at H900 specification. This decrease in hardness is a consequence of reformed austenite and overaged and underaged martensite that transform as a consequence of the high local heat applied during welding.

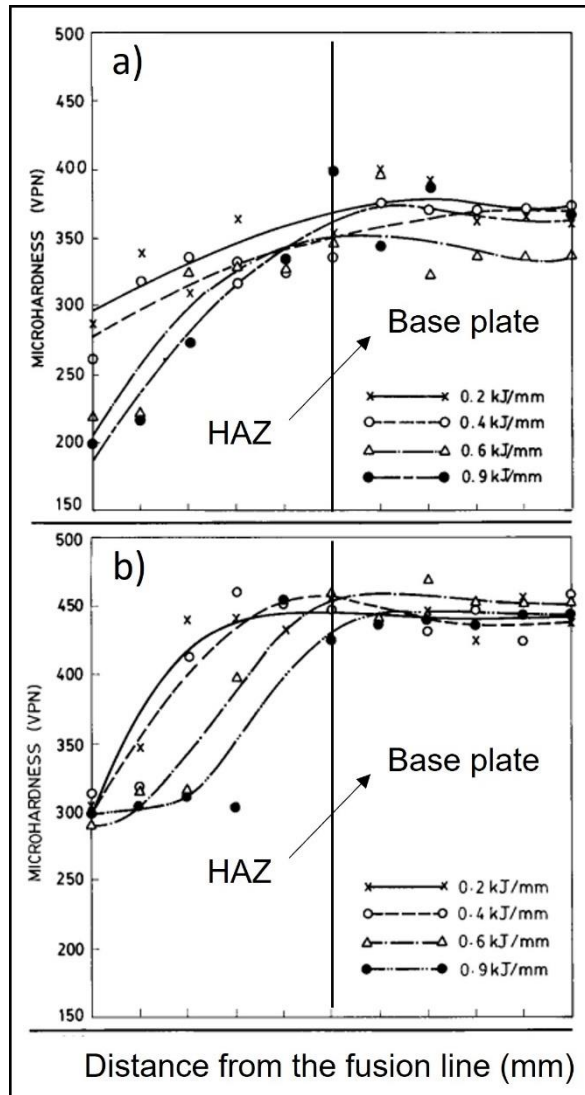


Figure 3-8. Microhardness profile across the HAZ of a 17-4 PH bead on plate weld: a) Condition A for the base plate; b) Condition H900 for the base plate [45].

Laser welding of 17-4 PH has also been explored to exploit the benefits of laser processing such as high energy density and deep penetration. From the literature, it has been established that one of the main concerns with the laser welding of 17-4 PH is the possibility of solidification cracking. It is commonly assumed that the risk for this type of cracking is low for 17-4 PH thanks to its δ -ferrite to austenite primary solidification mode [43]. δ -ferrite has a higher solubility for impurities such as phosphorus and sulphur as compared to austenite, allowing these species to readily dissolve into solid solution during solidification preventing their partitioning in the interdendritic regions and causing cracking [46]. However,

it has been identified that the higher cooling rates characteristic of laser welding can modify the primary solidification mode to an austenitic one instead, increasing the likelihood of hot cracking when combined with sufficient levels of residual stresses in the weld [47]. It is for this reason that it has been reported that cracking can generate at the centre line and root of the weld metal for example, when deep penetration (16 mm) hybrid laser-arc welding has been used, because of the high stress concentration at this region due to the high depth/width ratio [43]. In contrast, different research has reported that no cracking occurred during the laser welding of 17-4 PH when thinner plates and lower penetration (4 mm) were used [48]. This allows concluding, that even though 17-4 PH can be susceptible to hot cracking during laser welding, the generation of cracks or not depends on the geometric configuration of the weld, the developed stresses, and the welding parameters (heat input) used.

These findings on the arc and laser welding of 17-4 PH demonstrate that both the weld metal and the HAZ can have detrimental properties to the overall mechanical performance of the welded joint. Moreover, depending on the cooling rate and stress distribution, the risk of solidification cracking exists. Hence, it is important to investigate what is the effect that multiple heating cycles, such as the ones experienced during AM, can have on the stress distribution, microstructural features, mechanical properties, and defect generation of fused deposition of 17-4 PH.

3.2.6 Additive manufacturing of 17-4PH.

The 17-4 PH has been extensively investigated for AM applications thanks to its good availability and good combination of high strength and corrosion resistance. Most of the research has concentrated on the L-PBF of 17-4 PH. From the revised literature, it seems that cracking is not a common issue with the L-PBF of this alloy. However, higher percentages of retained austenite as compared to the forged material have been repetitively identified reaching values of more than 70% volume fraction of this phase [49]. Feedstock composition and processing conditions are the main factors controlling the amount of this generally undesirable phase. Hence, the development of 17-4PH AM applications has

concentrated on the control of the retained austenite and the post-deposition heat treatments to minimise its presence. **Figure 3-9** exemplifies why the retained austenite is normally not desirable in the final product. The strain stress curves show the discontinuous yielding for a sample with a high volume fraction of retained austenite (red curve) as a consequence of the strain-induced transformation from austenite to martensite [50].

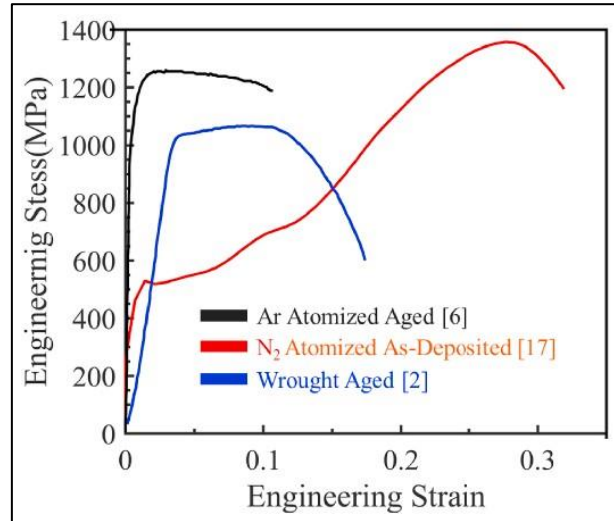


Figure 3-9. Stress-strain curves for various 17-4PH samples with different volume percentages of retained austenite. The red curve corresponds to a sample with a higher percentage of retained austenite as compared to the other two [50].

In terms of feedstock composition, it has been clearly established that the presence of nitrogen during powder atomisation or during the printing process will increase the amount of retained austenite on the final product as nitrogen is a strong austenite stabilising element. For example, it was reported that the content of nitrogen in the powder can go from approximately 0.01wt%, for argon-atomised powder, up to 0.12wt% for nitrogen-atomised powder. This increment was found to produce an increase in retained austenite from near zero to 81% [51]. Using nitrogen as a shielding gas in the deposition process can also increase the volume fraction of austenite in the final print. For example, when mechanical properties were compared when building samples by laser PBF under a pure argon atmosphere and pure nitrogen, it was found that the samples built under the nitrogen atmosphere exhibited a lower hardness as compared to the ones

built under argon after undergoing heat treatment. This was attributed to the higher capability of precipitation hardening in the martensitic microstructure in contrast to the matrix with retained austenite as a result of manufacturing with nitrogen [52]; showing that the shielding gas used can also have an important effect on the final mechanical performance. Apart from controlling the composition during manufacturing to limit the amount of nitrogen and hence the volume fraction of austenite, post-manufacturing heat treatment and its effect on the microstructure have also been investigated.

For L-PBF of 17-4 PH, studies on the effect of standardised heat treatments on the final mechanical properties have shown that they can be used to improve performance, but properties as high as the wrought counterparts cannot still be achieved [53,54]. Ageing alone was also shown to have a limited effect, as the solution treatment at high temperatures is required to break up the dendritic solidification microstructure and alleviate the microsegregation [53]. Despite the improvement in mechanical properties obtained after applying heat treatments, it has also been reported that if the amount of retained austenite is too high, this phase will remain, even after the two steps of heat treatment, and fully satisfactory properties cannot be achieved [51,55]. Proving once again the importance of controlling this phase in any of the manufacturing processes of 17-4 PH. The aforementioned findings, show the importance that feedstock composition and shielding conditions can have over the final properties of 17-4 PH printed using L-PBF. Nevertheless, this relationship has only been studied for this AM technology and it has not yet been extended to arc-based additive manufacturing methods.

In the field of arc-based additive manufacturing of 17-4 PH, only little effort has been dedicated to studying the WAAM performance of this alloy. Most of the, already limited, existing work, only focused on the defects generation and tandem deposition to increase deposition rates [56,57]. But no details were provided on microstructural features or the mechanical properties of WAAM deposited 17-4 PH. Only one previous study reports in more detail the “as-deposited” microstructure, which is formed primarily by martensite and a rather high-volume

fraction of retained austenite of 30%. It was also reported that satisfactory tensile properties were obtained by applying tailored post-deposition heat treatments that exceeded the properties of the wrought alloy [58]. It is worth mentioning that this work was completed at a later date as compared to Chapter 5 of this thesis, which is the section dealing with this topic. Even though this previous work gives a useful insight into the behaviour of 17-4 PH during WAAM, it does not include the effect of different shielding conditions and the influence of using different deposition strategies that can generate different microstructural features and properties of the deposited material. These aspects have been included as part of this thesis.

3.3 Near beta titanium alloy Ti-5553.

3.3.1 Introduction. Alloy classification, composition, and applications.

Ti-5Al-5V-5Mo-3Cr-0.5Fe %wt (Ti-5553) is a near- β titanium alloy which includes the addition of heavy β -stabilising elements to slow down solid-state phase transformation that can generate fine microstructural features of high strength up to 1517 MPa [59]. This is a relatively new titanium alloy and it has attracted attention since 2005, after it was selected for the manufacturing of large structural landing gear components on the Boeing 787 airframe [60]. This alloy possesses a better strength-to-weight ratio than Ti-6Al-4V and a wider processing window and deeper hardenability than its predecessor Ti-10V-2Fe-3Al [61]. For these reasons, Ti-5553 has been the focus of ongoing research to understand further the correlation between mechanical properties, microstructural features and manufacturing routes.

3.3.2 Production of Ti-5553. Common manufacturing route. Microstructure and mechanical properties of the wrought alloy.

Due to the addition of the beta stabilising elements, this alloy will remain almost fully β -phase at a lower temperature compared to other most commonly used titanium alloys such as Ti-6Al-4V. Since the BCC β -phase is softer and easier to deform plastically than the HCP α -phase, this allows for lower forging

temperatures which represent another of the great technical advantages of this alloy. Ti-5553 is mainly used in two microstructural conditions. The bi-modal microstructure or the fully lamellar. The former is the one normally obtained through thermo-mechanical processing (forging) and it can give a good compromise between high mechanical strength and ductility. The latter has the advantage of not requiring thermo-mechanical processing to be obtained but normally exhibits high strength values with brittle fracture behaviour. The common forging procedure applied to this alloy to obtain a bi-modal microstructure is represented schematically in **Figure 3-10**.

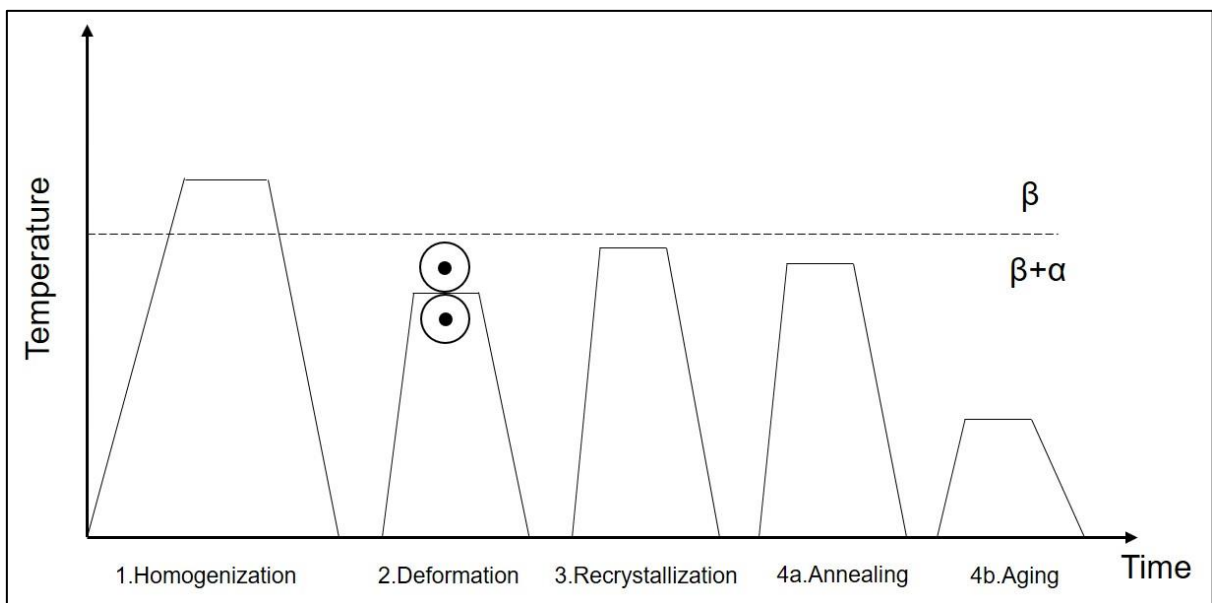


Figure 3-10. Schematic showing the processing steps of Ti-5553 to obtain bi-modal microstructure. Modified from [62].

During step 1, homogenization, the material is exposed above β -transus temperature. The cooling rate from this stage is critical as it will determine the thickness of grain boundary α (GB α) which is a continuous layer of α -phase at the grain boundaries. This phase is undesirable as it is detrimental to mechanical performance and cannot be fully avoided during the processing of Ti-5553. However, it can be minimised as the thickness of this layer is known to increase with decreasing cooling rate. One of the main advantages of the bi-modal microstructure in contrast to the fully lamellar is that, by creating a small enough

β grain size with the presence of globular primary α (α_p), the GB α only have a negligible effect on mechanical properties.

After the deformation stage, which is carried out under the β -transus temperature, a reheating stage for recrystallisation is applied. The recrystallisation temperature determines the volume fraction of α_p obtained which will affect the size of the recrystallised equiaxed β grains. The cooling rate from this stage is not critical as GB α will form on the smaller recrystallised β grains and their detrimental effect on properties is limited, as previously mentioned. The annealing stage 4a is applied to precipitate primary coarse α that will contribute to the strength of the material. Finally, the ageing treatment is performed at a lower temperature in order to precipitate the fine α -lamellae or secondary α (α_s) that will determine the total final strength of the alloy. A typical bi-modal microstructure after this processing route has been applied can be seen in **Figure 3-11**.

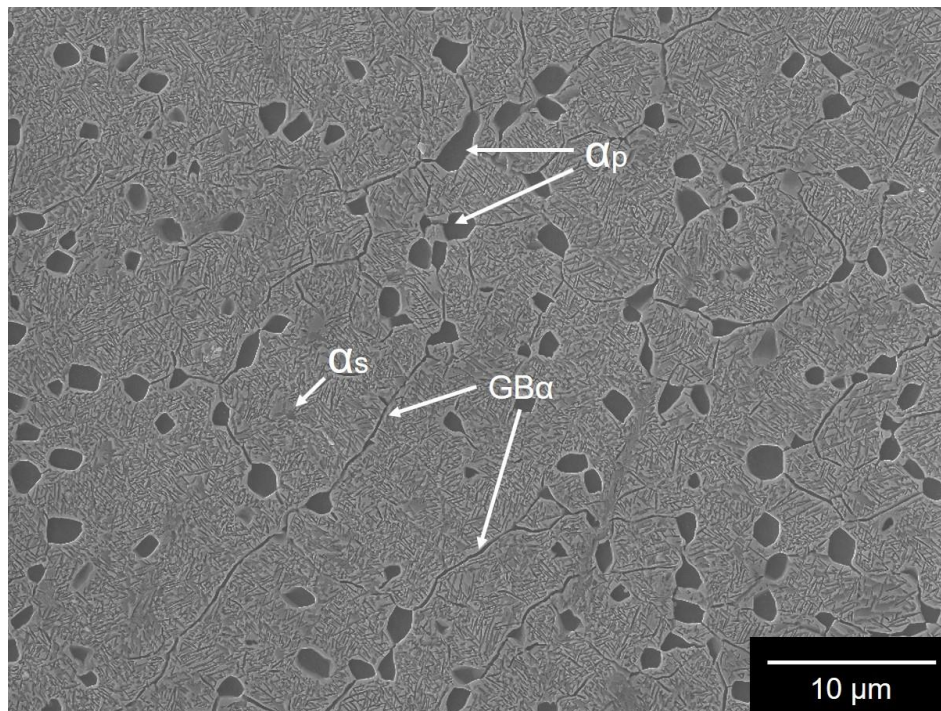


Figure 3-11. Typical bi-modal microstructure on Ti-5553. The various microstructural features had been indicated. α_p globular primary alpha phase, α_s secondary alpha phase (alpha lamellae), GB α grain boundary alpha.

To obtain a fully lamellar microstructure, the procedure is similar to the previously described for the bi-modal microstructure (**Figure 3-10**). However, the main

difference is that the recrystallisation stage 3 is performed above the β -transus temperature, this prevents the formation of the α_p phase. The cooling rate from the recrystallisation is important as it will determine the thickness of the GB α formed. Finally, the annealing and ageing stages are applied to form coarse and fine α -lamellae respectively which will determine the final mechanical strength of the alloy. A typical Ti-5553 fully lamellar microstructure after completing the heat treatment is shown in **Figure 3-12**.

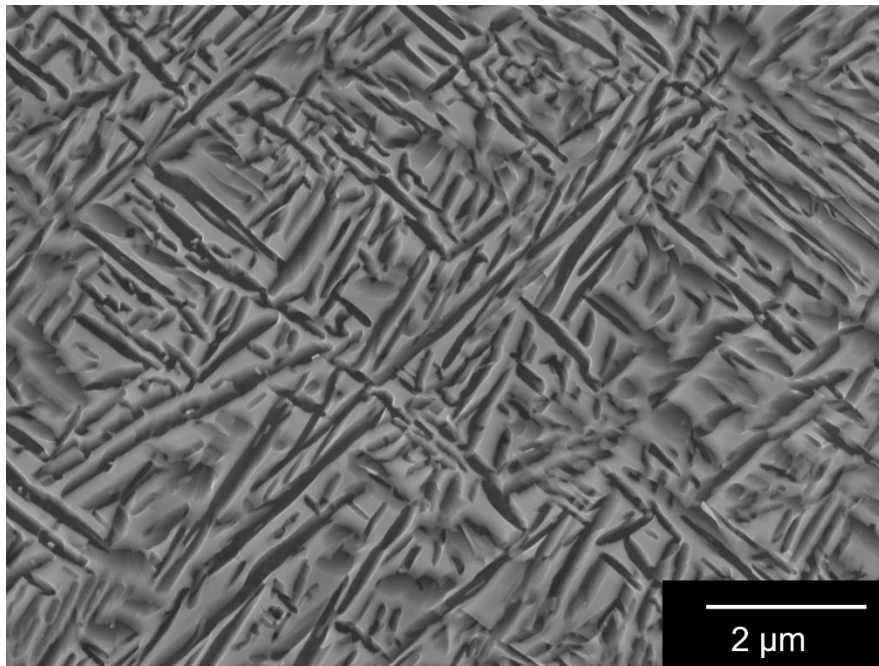


Figure 3-12. Typical bi-modal microstructure on Ti-5553.

Since the processing route to obtain bi-modal microstructures relies on the introduction of mechanical work into the material, it is not feasible to obtain these types of features during the WAAM processing of Ti-5553. Hence, fully lamellar microstructures are expected to be obtained as a consequence of the inherent cooling rates of the WAAM process and the reheating of previously deposited layers. For this reason, further literature review will be focused only on fully lamellar microstructures.

3.3.3 Physical metallurgy of Ti-5553. Response to heat treatment and non-equilibrium phase transformations.

The important microstructural features that determine the mechanical performance of Ti-5553 are the β -grain size, distribution and volume fraction of α -lamellae and the nature of the GB α . During traditional processing of Ti-5553, the β -grain size is determined by the amount of strain introduced during thermomechanical processing and also the recrystallisation temperature. However, the final mechanical strength in Ti-5553 is mainly determined by the α -lamellae phase mostly due to the formation of a large number of α/β interfaces that act as effective dislocation barriers.

The formation of the α -lamellae is the most complex solid-state transformation phenomenon that takes place during the processing of Ti-5553. The size, distribution and volume fraction of this phase depends mainly on the chemical composition and thermal history. Since the chemical composition is normally fixed, heat treatment is the method used to control this phase. The nucleation sites for the α -phase include prior β grain boundaries, secondary phase, such as the ω -phase, and dislocations. Hence, understanding the role of the of these secondary phases is of key importance, in particular the ω phase.

Athermal ω -phase precipitates upon quenching form above the β transus temperature. During subsequent isothermal aging at lower temperatures ($\sim 300^\circ\text{C}$), these precipitates coarsen to form chemically ordered ω precipitates together with the nucleation of the stable α -phase. On the other hand, aging at higher temperatures ($\sim 600^\circ\text{C}$) leads to dissolution of ω and further growth of the α precipitates accompanied by clustering of different α variants in self-accommodating morphologies [63]. Hence, it has been shown that aging temperature is key to the characteristics of the ω -phase that will later define the morphology and distribution of the α -phase.

Low temperature aging of Ti-5553 has been subject of various investigations as ω precipitates undergo coarsening and act as uniformly distributed heterogeneous nucleation sites for α precipitates. A consequence of this is that a relatively large number of a precipitates are formed and uniformly distributed

within the β matrix. Furthermore, these α -lamellae are of a relatively finer scale (usually nanometers to submicron) which gives excellent mechanical properties and often exhibit morphologies that are distinctly different from precipitates nucleated at higher temperatures. This difference in the ω -phase behaviour depending on the aging temperature has been attributed to the fact that the precipitation of ω particles only takes place on a very range of temperatures. Tang et al. [64] used precise dilatometry and transmission electron microscopy methods to determine that the ω -phase stability temperatures are between 275°C - 350°C. Hence, heat treatment routes must be carefully selected in order to exploit the α -lamellae refining capabilities of the ω -phase.

Due to the narrow and low temperature range of ω -phase stability, it has been found that a two-stage aging can be considered in order to refine the α -phase to the highest degree possible. For example, it has been reported that a two stage aging of Ti-5553 at 300°C and then 520°C can produce an excellent combination of high strength and satisfactory elongation [65].

Once the α -phase has nucleated, its growth is a diffusion-controlled process [63,66]. For this reason, time and ageing temperatures play an important role in the size and volume fraction of this phase. The size of the α -lamellae increases with both ageing time and ageing temperature [67]. This dependence can be seen clearly in **Figure 3-13**. Increasing ageing temperature leads to an increase in the length of the α -lamellae while increasing ageing time has a limited effect on further growth and gets saturated after the first two hours.

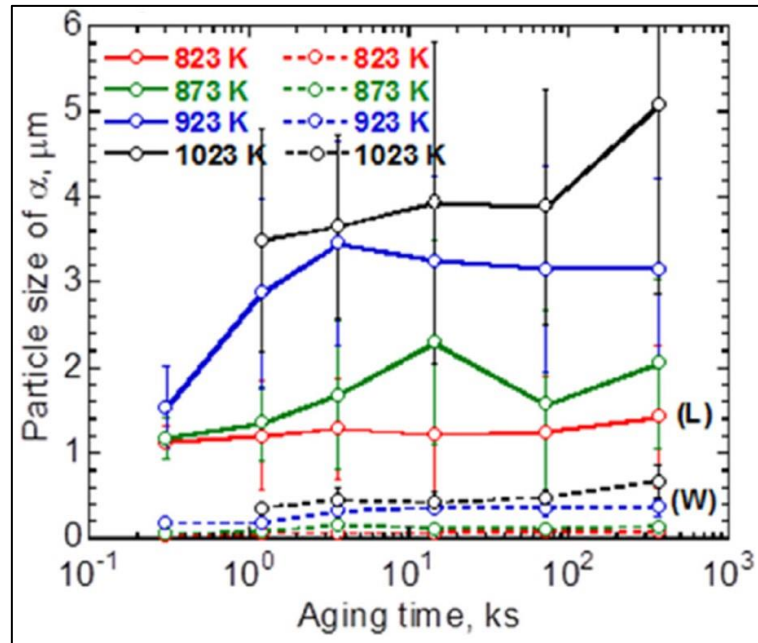


Figure 3-13. Effect of aging temperature and time on the length (L, solid line) and width (W, broken line) of the α -lamellae in Ti-5553 [67].

The volume fraction of α -phase also depends on the ageing temperature and time, but similarly to before, the temperature has a greater effect than the treatment time, as only a marginal increase is observed after an ageing time of approximately four hours. The volume fraction of the α -phase increases by decreasing the ageing temperature (**Figure 3-14**).

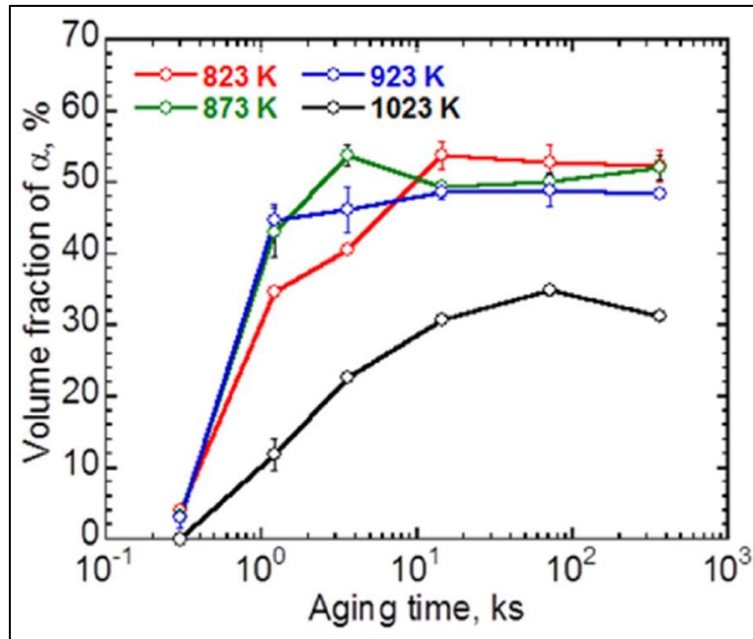


Figure 3-14. Effect of ageing temperature on the volume fraction of α -phase [67].

Apart from the response of Ti-5553 to heat treatment variables, it is also important to establish the correlation between non-equilibrium cooling conditions and the microstructural features developed. Specifically, the effect of cooling rates on α -phase transformations. **Figure 3-15**, shows the CCT diagram for Ti-5553 experimentally developed using dilatometry [68]. It can be seen in this diagram that cooling rates slower to $0.1\text{ }^{\circ}\text{C/s}$ will lead to the precipitation of the α -phase. For heating rates of $1\text{ }^{\circ}\text{C/s}$ or faster, the formation of α -phase will be surpassed and a microstructure of nearly 100% β -phase can be obtained. This is of particular importance for the understanding of the possible microstructural features than can be developed during various AM processes with different inherent cooling rates.

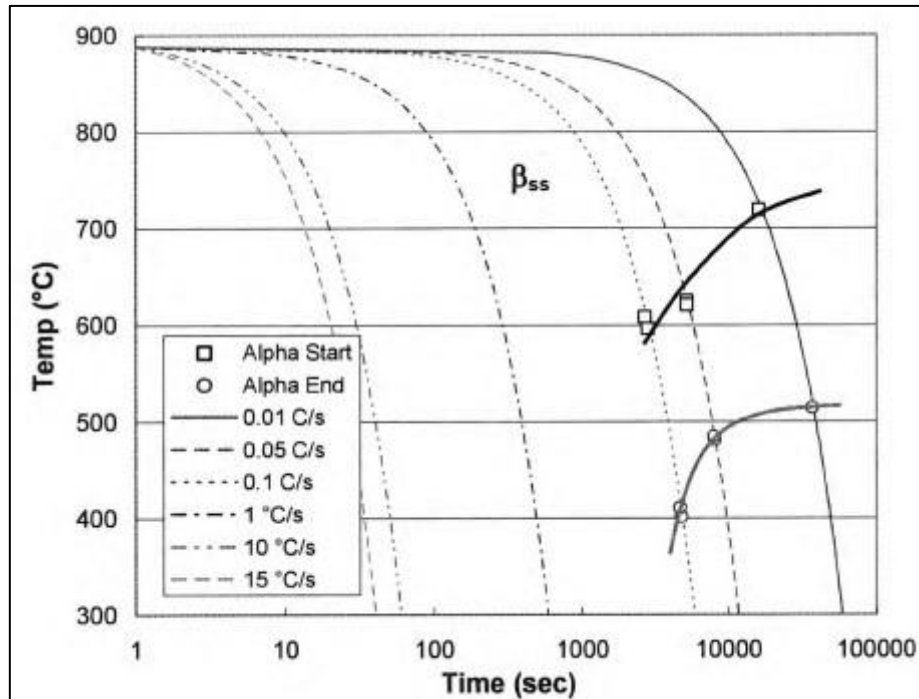


Figure 3-15. CCT diagram for bulk α -phase in Ti-5553 [68].

3.3.4 Welding of Ti-5553. Procedures and issues.

In order to exploit the full capability of Ti-5553 for aerospace applications, the response to various manufacturing routes, such as welding, has to be investigated. The weldability, as well as the microstructure and mechanical properties of the joints, has been reported in the literature for various welding technologies, including gas metal arc welding, laser welding and electron beam welding.

All of the consulted literature agrees that the same microstructural features can be identified in the welded joint despite the welding process used [69–72]. The fusion zone (FZ) is characterized by a coarse β -phase cellular-columnar grain structure that grows epitaxially from the semi-melted β -grains of the base plate (**Figure 3-16a**). Martensite is not identified in the FZ as the $[\text{Mo}]_{\text{eq}}$ for Ti-5553 is around 12, it has been established that martensite will not form for $[\text{Mo}]_{\text{eq}}$ values greater than 10 [69]. Sufficient time and temperature are not provided for the precipitation of the α -phase in this region. Hence, the FZ is nearly 100% retained β -phase. The HAZ close to the FZ is formed by coarse β -grains due to grain growth caused by the high temperatures at the proximities of the solid-liquid

interface (**Figure 3-16b**). On this region of the HAZ, the α -phase has been dissolved back to solid solution as the material has been heated above the β -transus temperature. The other portion of the HAZ, away from the FZ, exhibits a gradual transition to smaller equiaxed β -grains and an increasing volume fraction of α -phase moving towards the base plate (**Figure 3-16c**).

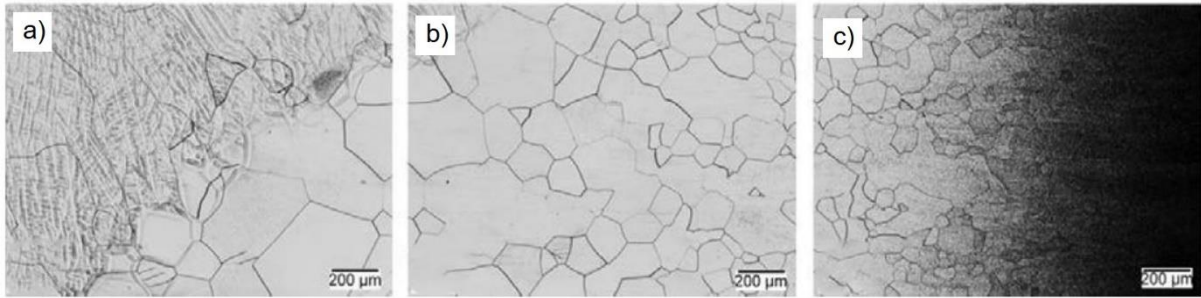


Figure 3-16. Microstructural features of a TIG welded Ti-5553 joint; a) Fusion zone; b) HAZ region close to FS; c) HAZ region away from the FZ and close to the base plate. Adapted from [69].

Even though the aforementioned microstructural features are found in all Ti-5553 welding, regardless of the process utilised, the weld profile and size will vary as a function of the heat distribution of the heat source and the welding parameters used, such as current/laser power and welding speed. This is expected, as different heat distributions of the heat source will generate a different profile on the material being welded. Gas metal arc welding and laser welding on a conduction regime tend to generate an elliptic melt pool following the arc heat source isotherms. On the other hand, laser and electron beam welding on the keyhole regime generates a bead profile with wide top and bottom parts with a narrow middle part, which is often referred to as an “hourglass” shape. This is believed to be due to Marangoni fluid flow at the top and bottom of the welds [69].

Since the FZ is formed mainly by only β -phase, the hardness and strength of the joint tend to be lower than that of the base plate, which is normally in the high strength aged condition. The final strength of the as-welded joints has been found to be around 76% of the strength of the base plate [71–73]. It is for this reason that some work has been dedicated to studying the effect of post-weld heat treatment (PWHT) on mechanical properties. For example, Zhang et al [71]

measured an increase of up to 98% in the strength of the base plate by applying a sub-transus solutionising treatment at 830°C and posterior ageing at 550°C for 7 hours. The improvement of the strength was attributed to the precipitation and growth of the α -phase in the FZ and HAZ which contributed to an overall increase of the strength of the joint. This highlights the importance of applying the correct heat treatment after the thermo-processing of Ti-5553 in the form of welding or even additive manufacturing processes.

3.3.5 Additive manufacturing of Ti-5553.

As it has been presented in this review, it is clear that the thermal history has a fundamental role in the metallurgical phases developed during the processing of Ti-5553. For this reason, it is expected that the repetitive thermal cycles characteristic of AM processes can have a significant effect on the final mechanical performance of additively built Ti-5553.

A review of the literature has revealed that the AM processing of Ti-5553 has been mainly focused on higher-energy-density laser and powder bed processes. In Chapter 6, previous investigations have been summarised identifying that the common feature of Ti-5553 deposited using laser and powder-based AM is the presence of a coarse and columnar β -phase grain elongated in the solidification direction together with no or limited amount of precipitated α -phase depending on the heat input utilised. A more detailed analysis of the published literature in this regard has been covered comprehensively in the introduction section of Chapter 6 of this thesis. The effects of arc and wire-based AM processes such as WAAM on the microstructural evolution and mechanical performance of Ti-5553 it is still very limited.

As it was shown in the previous section, PWHT is key to ensuring the satisfactory mechanical properties of welded Ti-5553. Since the microstructure will experience multiple thermal cycles during AM, this can make the obtained mechanical properties heterogeneous and unpredictable after additive manufacturing. It is for this reason that studying the effect of post-deposition heat treatments becomes paramount if AM is meant to become an alternative route to manufacture high-performance Ti-5553 components. However, from the revised

literature, only one study has considered the effect of post-printing heat treatment on the mechanical properties of Ti-5553. Hicks et al [74] obtained a near 100% β -phase microstructure in the as-deposited condition. Hence, in order to increase the strength, a solutionizing heat treatment was applied followed by ageing. Sub-micron α -lamellas were successfully precipitated, and the strength increased accordingly while the elongation results showed large deviations. It was found that such scatter in the plasticity data was a consequence of the formation of GB α during the heat treatment that led to brittle intergranular-transgranular fracture mode. Apart from this study, a pseudo heat treatment was applied by Schwab et al. [75] in the form of an in-situ heat treatment achieved by keeping the deposition substrate at a constant temperature of 500 °C. As a consequence of the extra heat supplied, precipitation of dispersed α -phase lamellas on the β -phase matrix was obtained producing a 52% volume fraction of the α -phase.

3.4 Interstitial elements on Ti-6Al-4V

3.4.1 Introduction. The high affinity for oxygen of titanium alloys. Technological problems of the high reactivity.

Titanium Ti-6Al-4V is used in many industrial applications as it provides excellent strength-to-weight ratios and good corrosion resistance at room temperature. However, Ti-6Al-4V is highly reactive to oxygen when it is exposed to temperatures higher than 450 °C. In fact, titanium is the material of engineering interest with the highest solubility for oxygen at 34at% [76]. Once this temperature is exceeded, oxygen atoms will diffuse into the bulk of the material modifying the microstructure and making the material more brittle. On the other hand, oxygen is not only detrimental to the mechanical properties as it can be used in a beneficial way as an alloying element to increase the mechanical strength and tribological properties of the material [77]. Hence, defining what are the acceptable oxygen concentrations limits in commercial components has always been a challenging task.

This high affinity of titanium for oxygen has caused that oxygen pick up is usually one of the main concerns in every manufacturing process involving titanium and different ways to eliminate or minimise it have been established. For example,

during the forging of titanium, severe oxygen pick up inevitably takes place at the surface of the parts, and they must undergo a chemical treatment called pickling, where the components are submerged in a solution of nitric and hydrofluoric acid in order to fully dissolve the oxidised material [78]. For welding and AM, since the material has to be fused, oxygen pickup is commonly minimised by providing an inert atmosphere using shielding gases such as argon and a huge effort has been invested in understanding how this can be achieved in the most efficient way. The need for these technological complications when processing titanium and their added cost have motivated the research to determine the role of oxygen in mechanical properties.

3.4.2 Effect of interstitial elements on Ti-6Al-4V microstructure and tensile strength and ductility.

Due to its small atomic radius, oxygen occupies the lattice interstitial sites when is in solid solution in titanium and its alloys. The presence of oxygen, and similar interstitials such as nitrogen and carbon, increases the c/a ratio of the α -phase, restricting the number of slip planes in the hcp structure, increasing the hardness and reducing ductility. Since oxygen content is known to modify the mechanical properties of Ti-6Al-4V, various researchers have focused on correlating the oxygen concentration levels with the tensile strength and elongation. In general, it has been reported that as oxygen concentration increases, the strength increases, while the elongation decreases. Despite of this dependence, it has also been reported that Ti-6Al-4V is not as sensitive to modifying its tensile behaviour with changes in oxygen concentration as compared to other titanium materials such as commercially pure (CP) titanium. This behaviour has been attributed to the fact that in the case of Ti-6Al-4V, the lattice strain has been already affected by the substitutional elements Al and V. These elements increment the c/a ratio and make any further increment, by the addition of oxygen, marginal [79]. **Figure 3-17** shows this behaviour where the c/a ratio has been plotted as a function of oxygen concentration for both Ti-6Al-4V and CP-Ti, the difference in the gradient is clear. The effect of various oxygen concentration levels on elongation has been discussed more in detail in Chapter 7 of this thesis.

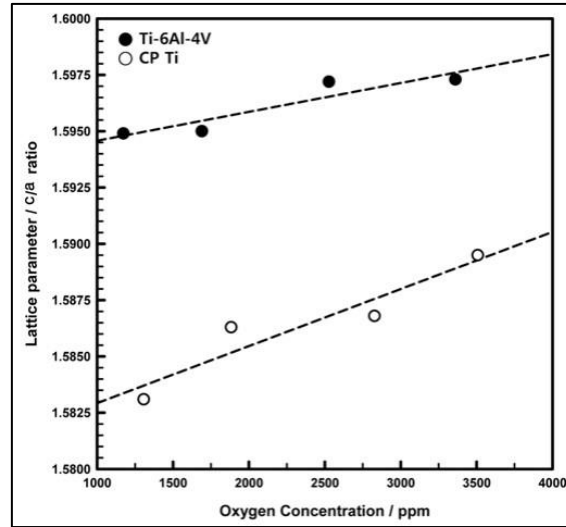


Figure 3-17. Comparison of the variation of c/a ratio between Ti-6Al-4V and CP-Ti [79].

In terms of microstructural changes, oxygen is an α -phase stabiliser element and, when the concentrations are high enough, it can suppress the formation of the β -phase. This leads to the formation of the well-known alpha case [80]. However, if the oxygen increment is within small limits, then microstructural changes are not that obvious at low magnifications. For example, it has been shown that for sintered Ti-6Al-4V powder, low magnification SEM micrographs revealed similar microstructural features for Ti-6Al-4V for an increment of oxygen content from 0.25 wt% to 0.49 wt% (**Figure 3-18a and b**). Conversely, higher magnification reveals that for the lower oxygen content, both α and β phases form a uniform solid solution phase free of precipitates (**Figure 3-18c**) while the sample with higher oxygen shows a considerable number of fine acicular precipitates (**Figure 3-18d**) [81]. In this study, the tensile properties were measured and the sample with 0.45 wt% had a decreased elongation of 12% as compared with the low oxygen counterpart. This demonstrates that even relatively small changes in oxygen concentration can produce observable changes in the microstructure that will affect the macroscopic properties.

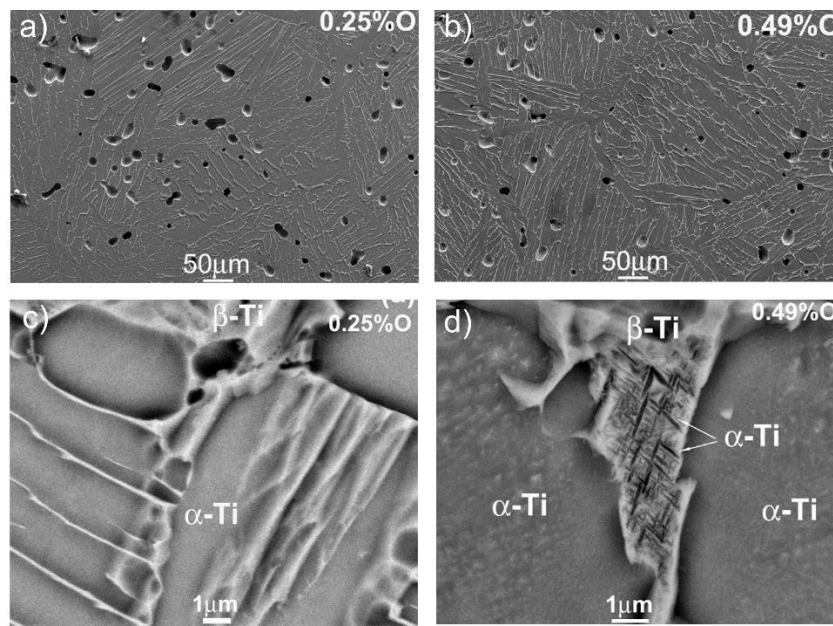


Figure 3-18. SEM-BSE of sintered Ti-6Al-4V with different oxygen content. a) and c) 0.25 wt%O₂, low and high magnification. b) and d) 0.49 wt%O₂, low and high magnification [81].

3.4.3 Oxygen pickup of Ti-6Al-4V during AM.

The effect of oxygen on the chemical composition and mechanical properties of Ti-6Al-4V during laser PBF has been reported. In this study, different levels of oxygen concentration in the samples were achieved by increasing the content of oxygen in the shielding atmosphere from 2 ppm to 1000 ppm. This translated into an increase in the oxygen content of the samples ranging between 1670ppm and 1848ppm, as compared to the initial oxygen concentration of the powder of 1308ppm. As the oxygen content increased an increment in the tensile strength was marginal at only 30MPa and elongation only dropped by 2.1% in total [82]. Hence, even though it was reported that a higher scatter was registered for higher oxygen levels, the overall effect on the properties of the samples by increasing oxygen content in the shielding was limited. These observations apply only as long as the oxygen is kept below 1000ppm in the building chamber, which seems to be the standard value used in commercial PBF machines. These are somewhat encouraging results since it has been established that a martensitic microstructure, such as the one found in laser PBF of Ti-6Al-4V, is more susceptible to severe embrittlement by oxygen additions [83]. However, in the

described study, the elongation was reduced but not significantly to the point of total embrittlement. This is in line with previous findings that have specified that a remarkable decrease in ductility is not expected for oxygen content levels below 2000 ppm [84].

Another similar study showed how the elongation can be greatly affected if the oxygen content of the shielding atmosphere during L-PBF is not carefully controlled. In this case, the built samples reached an oxygen content of 2200 ppm and the dropped in ductility went from 12% down to 6% [85]. Proving that even an increment of only 200 ppm, over the 2000ppm threshold for oxygen concentration levels, represented a significant difference in the ductile behaviour of the material. Hence, it is evident that controlling oxygen content remains an important factor to monitor and control during additive manufacturing of Ti-6Al-4V.

As previously mentioned, oxygen is an α -phase stabiliser element. Once that oxygen pickup takes places during the manufacturing process an oxygen enriched layer is formed near the surface. This oxygen concentration increase leads to the formation of the so call alpha case, which is a layer formed by high oxygen α -phase. This layer is normally undesirable as it is brittle and can lead to cracking and premature failure under cyclic loading [86]. For this reason, the alpha case formation on Ti-6Al-4V has been studied and characterised previously during WAAM deposition. It was reported that the alpha case thickness formed is mainly dependent on the thermal conditions of the samples during processing rather than on the oxygen concentration levels on the shielding atmosphere. However, the actual effect of increased oxygen content on the mechanical properties of the material were not considered [80].

3.5 Research gap

The literature has shown that despite the common belief that fibre laser sources are less sensitive to shielding gas composition, changing this process variable during L- PBF can and will affect the melting process behaviour. Hence, more research is required to elucidate the effect of shielding gas composition on

melting behaviour during L-PBF, especially for other materials and also under different experimental conditions as compared to the previously reported works.

The reviewed evidence on the manufacturing of Ti-5553 by AM suggests that the post-deposition heat treatment has an equally important effect on the mechanical properties as the thermal cycles during the manufacturing process do. However, this aspect has not been covered in the consulted literature for arc-based additively built Ti-5553. Therefore, the present study seeks to improve the understanding of this aspect of the arc processing of wire-based additive manufacturing of Ti-5553. In depth microstructural characterisation of this alloys under the manufacturing conditions of WAAM is also required as at present most of the available information is limited only to low heat input processes such as L-PBF. Knowledge of the starting microstructure under this condition is paramount in order to develop the suitable post deposition heat treatments in order to tailor and optimise the mechanical properties.

In the field of arc-based additive manufacturing of 17-4 PH, only little effort has been dedicated to studying the WAAM performance of this alloy. Most of the available knowledge only limits for powder-based processes. Even though this previous work gives a useful insight into the behaviour of 17-4 PH during additive manufacturing of 17-4PH, it does not include the effect of different shielding conditions and the influence of using different deposition strategies that can generate different microstructural features and properties of the deposited material. These aspects have been included as part of this thesis.

As it has been shown, most of the previous work has covered mainly the role of oxygen and oxygen pickup during L-PBF and these mechanisms have not been extensively described for the WAAM process. Additionally, the role of oxygen coming from the oxygen pickup inherent to the AM process through the shielding conditions it is what has been covered so far. But no previous research has systematically studied what is the correlation between oxygen concentration in the wire feedstock and the final mechanical properties obtained. Hence, it is part of the present thesis to explore this aspect with the intention of shedding some

light on the accepted oxygen content tolerances for Ti-6Al-4V manufactured by WAAM.

3.6 References

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4 Effect of shielding conditions on bead profile and melting behaviour in laser powder bed fusion additive manufacturing.

This chapter is based on the following publication.

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The first step of this research was to investigate if a correlation between laser-material fundamental interaction parameters and bead profile could be established. This with the aim of printing satisfactory mechanical properties through the proper control of bead geometry that could lead to the elimination, or at least mitigation, of volumetric defects. Previous work at Cranfield was able to achieve this for laser welding and the same approach wanted to be extended for laser powder AM. However, initial trials revealed that using the industry's standard shielding gas, argon, leads to severe process instabilities and random fluctuation between melting modes. This made it impossible to establish any relationship between melting parameters and bead geometry. By identifying the right shielding conditions using helium and a cross flow, it was possible to control the bead profile and establish a correlation between melting parameters and bead geometry obtained. Hence, this publication was prepared to summarise such findings on the criticality of shielding gas composition of the stability of the laser powder bed fusion process.

Abstract: a series of experiments were performed using a 500W continuous wave fibre laser on a single powder bed layer using different processing variables. The aim was to investigate the effect of different shielding conditions on melting behaviour and bead profile in laser powder bed fusion (PBF). Through high-speed imaging, it was found that under an argon atmosphere, a strong plasma plume is generated from the melt pool. Laser beam-plasma plume interactions caused strong instabilities during melting, including laser wandering,

track instability and continuous fluctuations between melting regimes (conduction and keyhole). Hence, it was not possible to control the profile of the melted tracks under this condition. By using a helium atmosphere, a smaller plasma was obtained, reducing the disruptions caused by laser-plasma interactions. This led to a stable melting regime that allowed control of the melt bead profile. This condition was used to study the effect of laser-material fundamental interaction parameters on the bead geometry in powder bed melting. It was found that during the melting of single tracks, the dominant regime of melting is conduction for the range of parameters tested. Penetration and melt width were found to increase with increasing energy density. For longer interaction times, melt widths were found to be up to ten times the size of the beam diameter used. Fluid flow modelling showed that this is due to strong melt flow as a consequence of surface tension gradients generated by very high-temperature gradients.

Keywords: powder bed fusion, plasma plume, argon atmosphere, helium atmosphere, SLM.

4.1 Introduction.

Laser powder bed fusion (L-PBF) is a powder-based AM technology that has attracted increasing attention in the recent years. In L-PBF, high complexity and high resolution parts can be obtained through the selective melting of successive layers of metallic powder using a laser beam [1]. Additional advantages of PBF include improved design flexibility and shorter lead times as compared to traditional technologies [2]. During the powder-laser interaction, many physical phenomena take place, making it difficult to control the quality of manufactured parts. Such phenomena include material vaporization and complex gas dynamics, which are known to cause defects in the final component [3]. The most common defects are porosity and lack of fusion, which can compromise the structural integrity of a component. For this reason, the effect of numerous process parameters on the melting behaviour and bead geometry on PBF has been the subject of many investigations in order to minimise the occurrence of such defects.

As a way to mitigate defect formation during PBF, it is useful to establish the correlation between processing conditions and the bead profile obtained. Additionally, the control of bead shape is important because it determines the resolution and layer height achieved in the process. It is known that for laser welding and other AM techniques, the shielding conditions used can have an important effect on the melting behaviour, geometry and microstructure of the manufactured parts [4,5]. Hence, it is expected that optimising the shielding atmosphere during PBF could have a significant impact on the process characteristics and can be used as a way to control the bead profile and minimise defects.

Several studies have been performed regarding the role of the shielding gas during laser welding, particularly the effect of argon and helium. Most of the published work agrees on the fact that laser welding under helium or higher percentages of helium leads to a smaller plasma plume volume and also enhanced melting stability [6,7,8]. This has been attributed to the better cooling effect of helium as compared to argon and to its higher ionization potential. Previous works have also come to the conclusion that for CO₂ lasers ($\lambda = 10.64 \mu\text{m}$) the total absorption in the plasma plume of the laser radiation can be up to 33% when argon is used and only 5% when helium is used instead. Hence, it has been reported that, for CO₂ laser beam welding, shielding gas composition has an important influence on weld penetration where deeper weld penetration has been obtained by increasing the content of helium [9,10]. In contrast, it has been found that for lasers of shorter wavelengths such as YAG, fibre or disk laser ($\lambda = 1.064 \mu\text{m}$) the effect of shielding gas on process stability and weld geometry is minor and other parameters such as laser power density are dominant. For example, Kuo and Lin [11] reported that for a fixed set of welding parameters, similar penetration shapes and depths are obtained independently of the shielding gas employed. This is due to the fact that during Nd:YAG laser welding, laser energy absorption in the plume is very weak and therefore the plume volume has a lesser influence on the penetration depth. The effect of different shielding gases on melting stability for fibre laser in combination with small beam

size ($\leq 100 \mu\text{m}$), such as the ones commonly used in laser PBF, needs to be further explored.

For additive manufacturing, there has not been much work focused on the role of shielding gas on process characteristics. Bidare et al [12] reported that, in contrast to using argon, a helium atmosphere gives more stable melting that produces a smoother surface finish of the melted tracks, but increased depletion of powder particles away from the processing point was observed. However, this work was mainly focused on the study of PBF under a high-pressure argon atmosphere with little attention to melting behaviour and bead geometry. Their work did not show any particular benefit from using high-pressure atmospheres, as compared to atmospheric pressure. Montgomery et al [13] considered the implementation of different shielding gases and their effect on surface finish. It was found that the powder morphology is the controlling factor for the surface finish rather than the gas composition. In other studies, such as Zhou et al [14] and Bidare et al [15], powder melting under vacuum conditions was investigated. The former found reduced porosity in PBF of Ti-6Al-4V while the latter reported a limited reduction in spatter generation at expense of an increase in denudation of the powder. A feasible method to visualise the shielding gas flow during PBF melting has also been covered by Schniedenharn et al [16]. However, the influence of the gas flow and type on the bead profile was not reported.

Knowing the bead geometry that corresponds to a particular set of processing parameters is paramount to develop a robust process for printing of high quality parts. For this reason, many researchers, such as Guo et al [17] and Shi et al [18] have reported the changes in layer height, penetration depth and bead width as a function of laser power and scanning speed. However, most of the work focuses only on processing under argon atmosphere and no alternative gases have been studied. For this reason, the effect of processing parameters, such as laser power and scanning speed on bead geometry are investigated in this work when helium is used as shielding gas. Additionally, the potential of increasing deposition rates during PBF has been explored in the present work by the implementation of a relatively large beam size and thicker powder layer as compared to commercial

systems. As shown previously by Shi et al [18], building rates can be increased up to 9 times by using powders layer and beam sizes around 200 μm as compared to commercial equipment.

4.2 Material and Methods

4.2.1 Materials and experimental system.

An in-house developed powder bed fusion test rig was used for this work (**Figure 4-1**). This system is an open architecture design that allows the installation of different laser systems and instrumentation. To exclude any source of distortion and instabilities to the projected laser spot by a galvo scanner, a standard welding head was used and the powder bed was moved using a set of high precision x-y linear stages. The powder test rig was enclosed inside an airtight chamber and the oxygen level was controlled by using an Microx Ntron oxygen analyser. High-speed imaging of powder processing was captured using a “Phantom” Vision Research camera fitted with a 25mm-f/1.4 lens. The resolution used was 640x480 pixels at 1000 fps. The entire camera was installed inside the chamber to achieve close-up views.

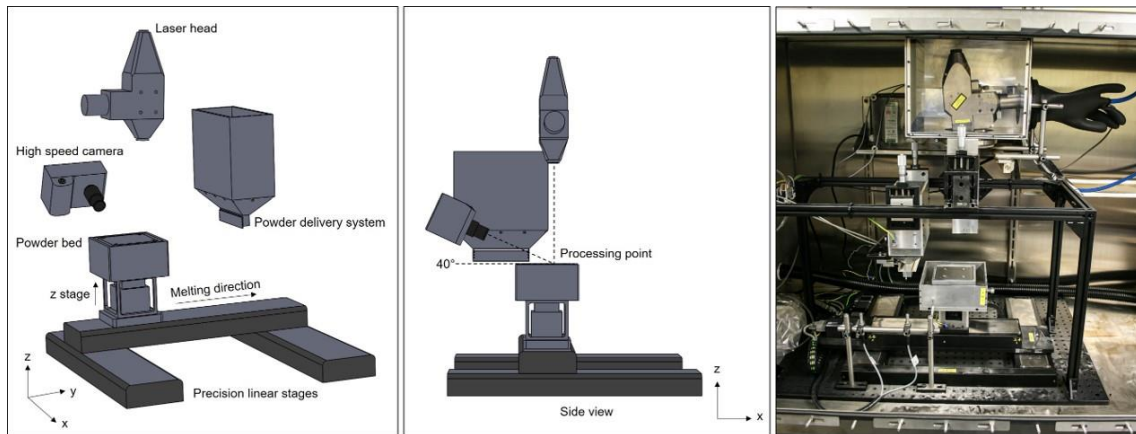


Figure 4-1. Schematics of powder testing rig and experimental set up.

A continuous wave fibre laser with a maximum power of 500 W and $\lambda = 1064\text{ nm}$ was used. The laser beam was delivered through an optical fibre of 50 μm diameter, collimated with a 300 mm focal length lens. Laser light with a Gaussian intensity distribution was used at the focal point giving a $D4\sigma$ diameter of 100 μm . All experiments were carried out with the focal point on the surface of the powder

layer, or workpiece in the case of solid substrate. To prevent back reflection, the laser head was tilted 5° backward with respect to the travelling direction.

For the melting trials, single tracks with a length of 70 mm were produced. Experiments were performed on powder and solid substrates using the same set of parameters in order to study the melting behaviour in both powder and solid. All powder melting carried out was performed using gas-atomised stainless steel 304L powder with a particle size range of 45-75 µm ($d_{10}=41.5\text{ }\mu\text{m}$, $d_{50}=56.9\text{ }\mu\text{m}$, $d_{90}=77.4\text{ }\mu\text{m}$). A single powder layer of a thickness of 250 µm was used. This thickness was higher than the ones normally used in L-PBF which are normally around 40µm due to the limitations of the powder testing rig used. However, this investigation was aimed at understanding the laser-material interaction fundamentals instead of replicating the “standard” conditions used in commercial systems. Powder recoating was achieved by a gravity-fed system using a polytetrafluoroethylene scraper to remove the excess powder. 304 stainless steel with dimensions 12 mm x 85 mm x 85 mm was used as base plates.

Suder and Williams [19] successfully applied a system-independent approach that allowed identification of the parameters controlling the bead geometry for keyhole laser welding. This approach is based on the implementation of a set of fundamental laser-material interaction parameters. These parameters fully determine the material response to the laser energy independent of the laser system used. In this work, the same approach was followed and power density, interaction time and energy density were used to establish the dependence of bead geometry to process system parameters (laser power, scan speed and laser spot size). These parameters are defined as: Power density, $PD = P/A_{beam}$ (kW/cm²), Interaction time, $t_i = D_{beam}/TS$ (ms) and Energy density $E_d = PD \cdot t_i$ (kJ/cm²) Where P is the laser power used. A_{beam} is the laser beam area projected on the surface. TS is the travel speed and D_{beam} the laser beam diameter used.

In order to determine how these parameters control the melt profile in laser PBF, a range of power densities of 4800, 5500, 7100 and 7700 kW/cm² were tested together with interaction times ranging from 0.35 ms to 4 ms, which corresponds to a scanning speed of 257.1 mm/s and 22.5 mm/s respectively. Higher scanning

speeds were not tested on this work as the motion system of the in-house developed laser powder bed testing rig was based on a set of linear stages that had a maximum movement speed of around 270 mm/s. The idea of using linear stages instead of a galvo scanner was to avoid changes in the beam shape at the processing surface (e.g. elongation of the beam) that can alter the spatial energy distribution and have a significant influence on the resultant melt bead geometry.

4.2.2 Testing sequence of different shielding conditions.

Initially, melting of powder and solid was performed using commercially pure argon gas (99.998% Argon). The argon inert atmosphere was created by pumping the gas into the air-tight chamber until a concentration of 300 ppm of oxygen was achieved. This condition will be referred to as “global shielding” in this work. No additional flow of gas was induced.

Subsequently in some experiments, additional cross-flow shielding on top of the argon global shielding was used to suppress the plasma. A Meech A85006 commercially available air knife of 150 mm long with an argon gas input pressure of 2.5 bar was used to apply a cross-flow gas over the powder bed. The stand-off distance between the air knife and the powder bed was 15 mm. This is referred to as “global argon with cross flow” setup. These trials were designed with the aim of determining how localised control of the plasma plume affects melting behaviour and the laser beam-plasma plume interactions. A simplified diagram of the relative position of the cross-flow with respect to the powder bed is presented in **Figure 4-2**.

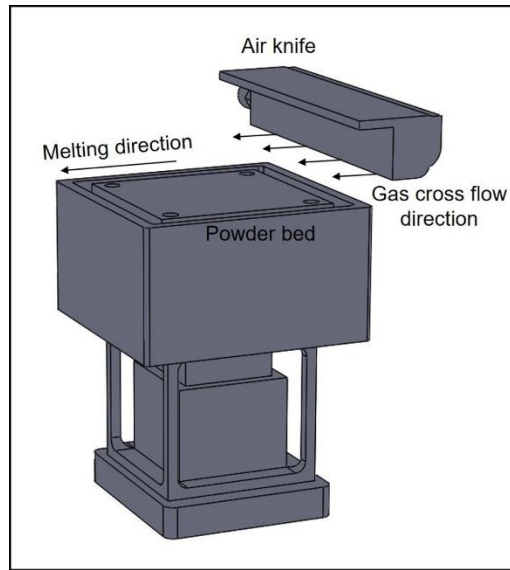


Figure 4-2. Experimental setup for the gas cross flow.

In the final experimental stage, melting of powder and solid was performed in a global helium gas inert atmosphere without cross flow, just using a global shielding atmosphere with the same processing conditions previously used for the global argon shielding.

4.2.3 Sample processing.

Cross-sections of the single tracks were produced to analyse the effect of the different processing conditions on melt geometry. Cross-sections were taken at halfway of the length of each track and were mounted in cold resin. In order to establish the relationship between plasma plume characteristics and bead shape, a careful correlation between the still images and a particular cross-section was established. In order to achieve this, a particular location of the melt track was located on the still image. Subsequently, the distance from there was calculated using the time interval. In the example presented in this work (**Fig. 4-5**) the time intervals were equivalent to distances ranging from 1 mm to 4 mm from the initial reference point. Hence, it was possible to locate a specific melt track location by carefully grinding away the required amount from the resin-mounted sample. Samples were ground and polished following standardised procedures for metallographic preparation of austenitic stainless steel. Etching was performed using Kalling's 2 reagent. Measured dimensions are schematically indicated in

Figure 4-3, where the aspect ratio is defined as the results of the penetration depth over the bead width. Profiles were imaged using optical microscopy.

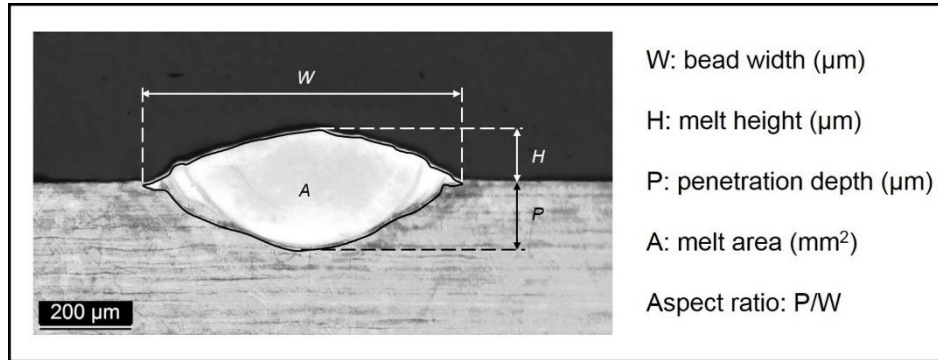


Figure 4-3. Macrograph of track cross-section defining the measured bead outputs. “Melt height” applies only in the case of powder melting.

4.2.4 Numerical simulation.

To investigate the formation mechanism of certain bead geometries, two-dimensional transient fluid flow numerical simulations were made based on the widely used commercial CFD-software Ansys-Fluent. In the simulations, the single-phase laminar fluid flow module was used together with the heat transfer module due to the near flat bead shape obtained from the experiments. The actual fibre laser beam profile was approximately a Gaussian distribution. Thus, a surface Gaussian heat source considering the travel speed was used in the simulations [20]. To simplify the model, the plume was not incorporated. The absorption coefficient of the laser was set as a fixed value of 0.2 [20]. In the two-dimensional model, wall boundary conditions were employed as the momentum boundary. Marangoni stress was applied on the top side while no-slip boundary conditions were applied on the other three sides. For the energy boundary, the Gaussian surface heat source was applied to the top sides. Besides, the heat convection and radiation with the environment were considered in the other three sides. The convective heat transfer coefficient used was $80 \text{ W}(\text{m}^2\text{K})$ and a surface radiation emissivity of 0.4. To make the calculation more tractable, only a small size of the specimen, $1.5 \text{ mm} \times 0.6 \text{ mm}$, was employed in the simulations. A small uniform mesh of 0.005 mm , which is only one-tenth of the radius of the laser spot, was used. A fixed time step of $5 \times 10^{-7} \text{ s}$ was set to calculate to be

great convergence. The melting parameters are the same as that in the experiments (power density of 5500 kW/cm²). The physical parameters of the base plates (304 stainless steel) are shown in **Table 4-1**.

Table 4-1. Physical parameters of 304 stainless steel used in the simulations
[21,22,23]

Property	Symbol	Value
Liquid density (kg m ⁻³)	ρ_l	7200
Liquid specific heat(J kg ⁻¹ K ⁻¹)	C_p	760
Liquid heat conductivity (W m ⁻¹ K ⁻¹)	k	35
Solidus temperature (K)	T_s	1670
Liquidus temperature (K)	T_l	1727
Boiling temperature (K)	T_v	3375
Melting latent (J kg ⁻¹)	L_m	2.47×10^5
Evaporation latent (J kg ⁻¹)	L_v	6.52×10^6
Liquid dynamic viscosity (N m ⁻² s)	μ_l	0.006
Liquid coefficient of thermal expansion (K ⁻¹)	β	1.96×10^{-5}
Surface tension temperature coefficient (N m ⁻¹ K ⁻¹)	$\frac{d\sigma}{dT}$	-0.43×10^{-3}

4.3 Results.

4.3.1 Argon global shielding.

Cross-sections of some selected melt profiles produced using argon global shielding are presented in **Figure 4-4**. From the images, it can be seen that the behaviour of the melt pool fluctuates in terms of melting regime. That is, for the same power density, melt profile fluctuates between conduction and keyhole regimes as the interaction time is increased. This was found to be the case for both powder and solid melting as shown in **Figure 4-4a** and **Figure 4-4b** respectively. Note that the change of process regime and resulting bead shape changed randomly for both cases. In many instances, particularly for longer interaction times, the melt profile width was found to be up to ten times greater than the beam size used. This indicated strong convection in the liquid.

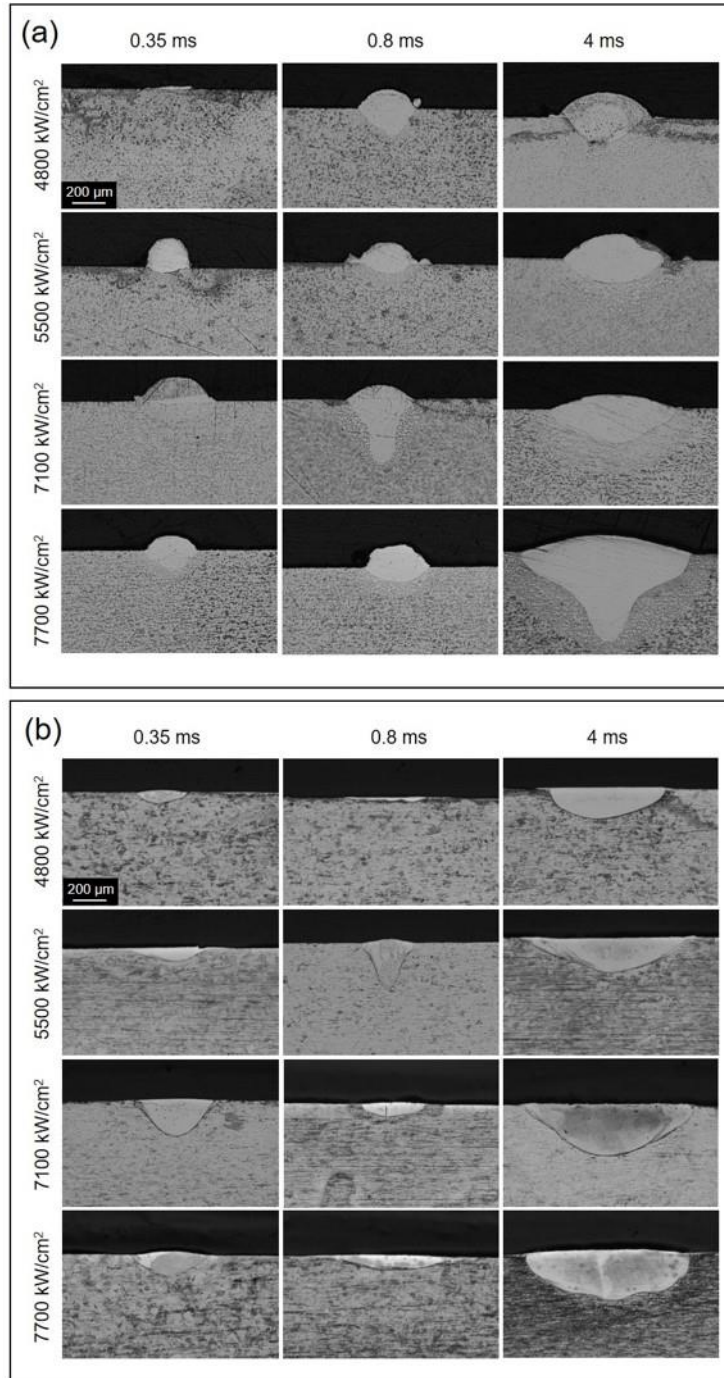


Figure 4-4. Selected cross-section from single tracks using argon shielding for different combinations of power densities and interaction times. (a) Powder melting. (b) Solid melting. Beam size: 100 μm.

Figure 4-5, shows the relationship between plasma plume behaviour and penetration depth for the same set of parameters. It can be observed that fluctuations in the plume characteristics occur with a change in the melting regime. More specifically, it was found that a high intensity plasma plume with high upward directionality is associated with the keyhole regime with a deep penetration bead profile. While a small visible surface emission corresponds to the conduction regime with a characteristic hemispherical bead profile.

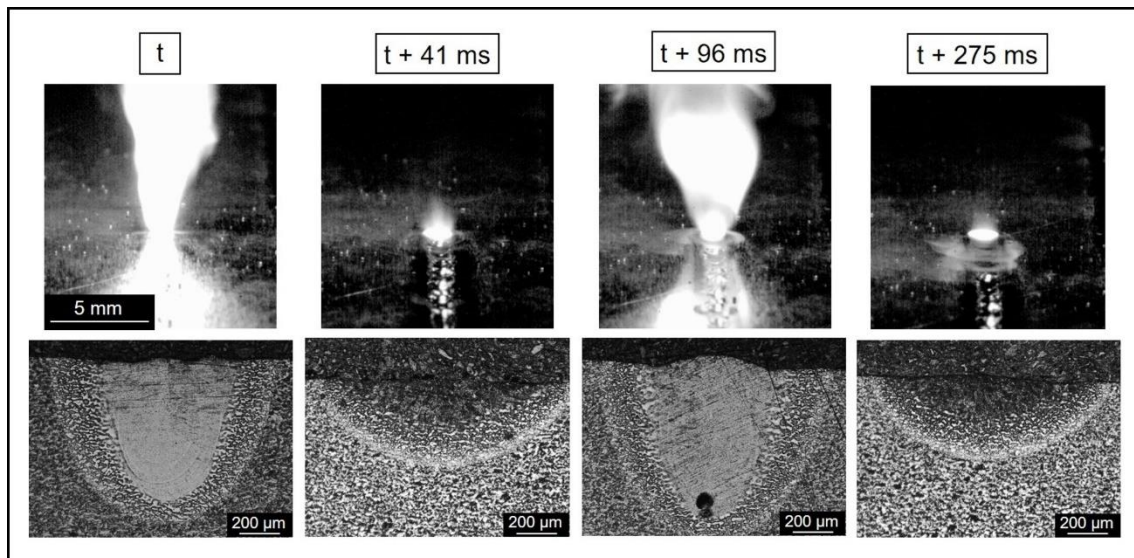


Figure 4-5. Correlation between plasma plume characteristics and penetration depth for the same track. Power density 7700 kW/cm², Interaction time 4 ms, solid melting.

Figure 4-6a-b, show stills from the high-speed imaging, highlighting the previously described plasma plume behaviour. **Figure 4-6c** provides a different angle view, where the effect of plume fluctuation on the track linearity can be observed. In some instances, the change in plume behaviour is accompanied by wandering of the melt track. These changes in plume characteristics were found to occur at random locations along the melt track.

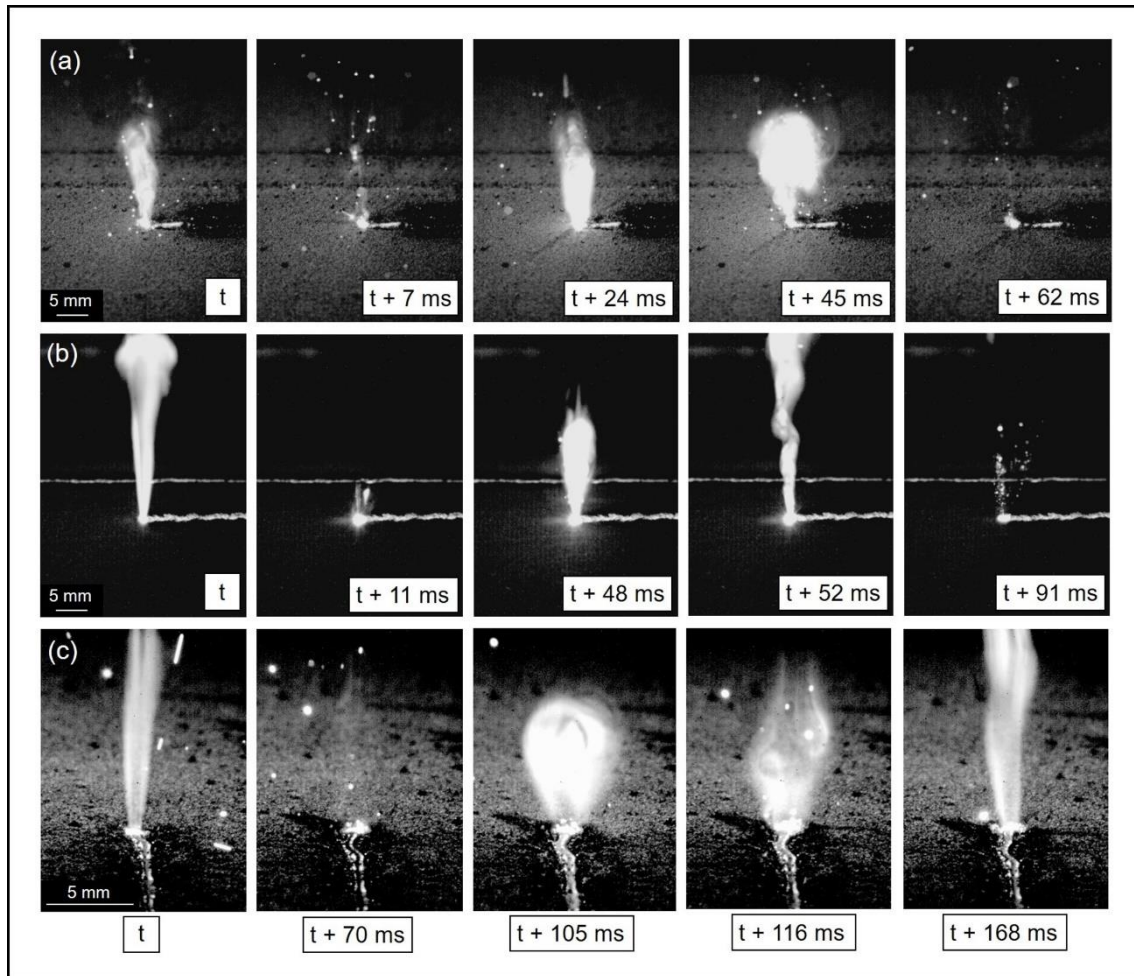


Figure 4-6. High-speed images for single tracks melting using global argon shielding with a power density of 4800 kW/cm² and an interaction time of 4 ms. (a) Side view of melting of powder. (b) Side view of melting of solid substrate. (c) Front view of melting on powder.

4.3.2 Global argon shielding with cross flow.

High-speed imaging of powder melting performed with an argon cross-flow setup together with global argon shielding for two different interaction times are shown in **Figure 4-7**. When a gas cross-flow was added, fewer fluctuations of the plasma plume were observed, leading to more stable melting. Additionally, the size and intensity of the laser-induced plasma decreased in the presence of the cross-flow.

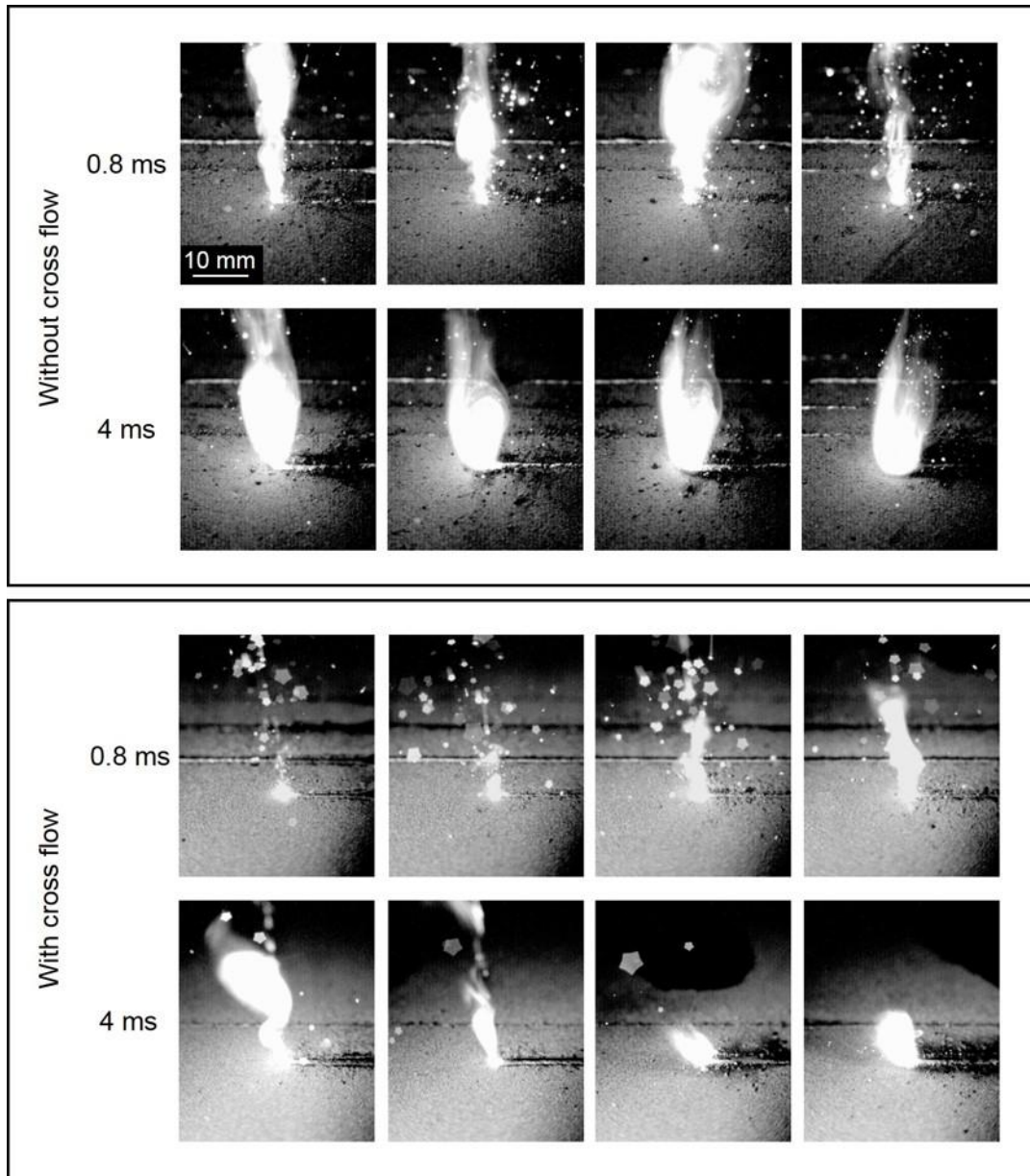


Figure 4-7. High speed imaging of powder melting without and with argon gas cross flow and global shielding for two different interaction times. The time intervals between snapshots are 155 ms and 775 ms for interaction times of 0.8 ms and 4 ms respectively. Power density: 7700 kW/cm².

4.3.3 Helium global shielding.

In the next experiment, global helium was used. **Figure 4-8** shows selected cross-sections from single tracks produced under global helium shielding and with the same parameters as in **Figure 4-4**. A consistent melting regime can be identified in contrast to the profiles obtained using global argon shielding. In this

case, the conduction melting regime is present with no fluctuations between conduction and keyhole. This behaviour is verified for both powder and solid melting. It can also be seen that penetration depth increases with power density and interaction time. This gives foundation to the potential development of processing algorithms for control of bead profile and hence resolution, quality and remelting in powder melting. The width is fixed and proportional to the spot size for short interaction times, but then increases significantly, as the interaction times get longer. A detailed look at **Figure 4-8a** reveals that no powder consolidation was obtained for power densities of 7100 kW/cm^2 and 7700 kW/cm^2 when short interaction times were used. The maximum bead width was found to be around $1200 \text{ }\mu\text{m}$ for helium global shielding, while the maximum width for argon shielding was around $1000 \text{ }\mu\text{m}$. This means that even wider beads are obtained when using helium as compared to argon shielding gas, which can be attributed to strong convection in the liquid metal.

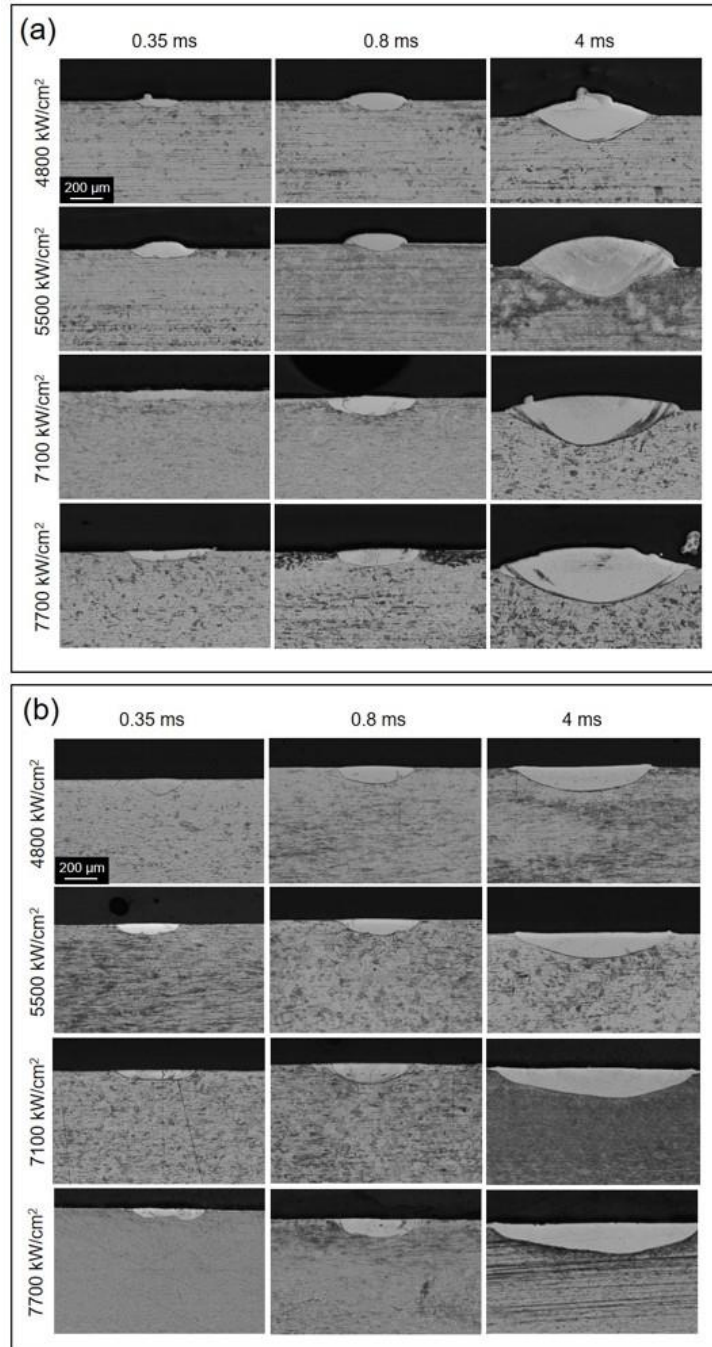


Figure 4-8. Selected cross-sections from single tracks using global helium shielding for different combinations of power densities and interaction times. (a) Powder melting. (b) Solid melting. Beam size: 100 μm .

During melting under a helium atmosphere, high-speed imaging revealed that the plasma plume is smaller and of less intensity compared to melting under argon atmosphere for the same set of processing parameters (**Figure 4-9**). Additionally, less plasma instability and fluctuation are seen for helium compared to argon.

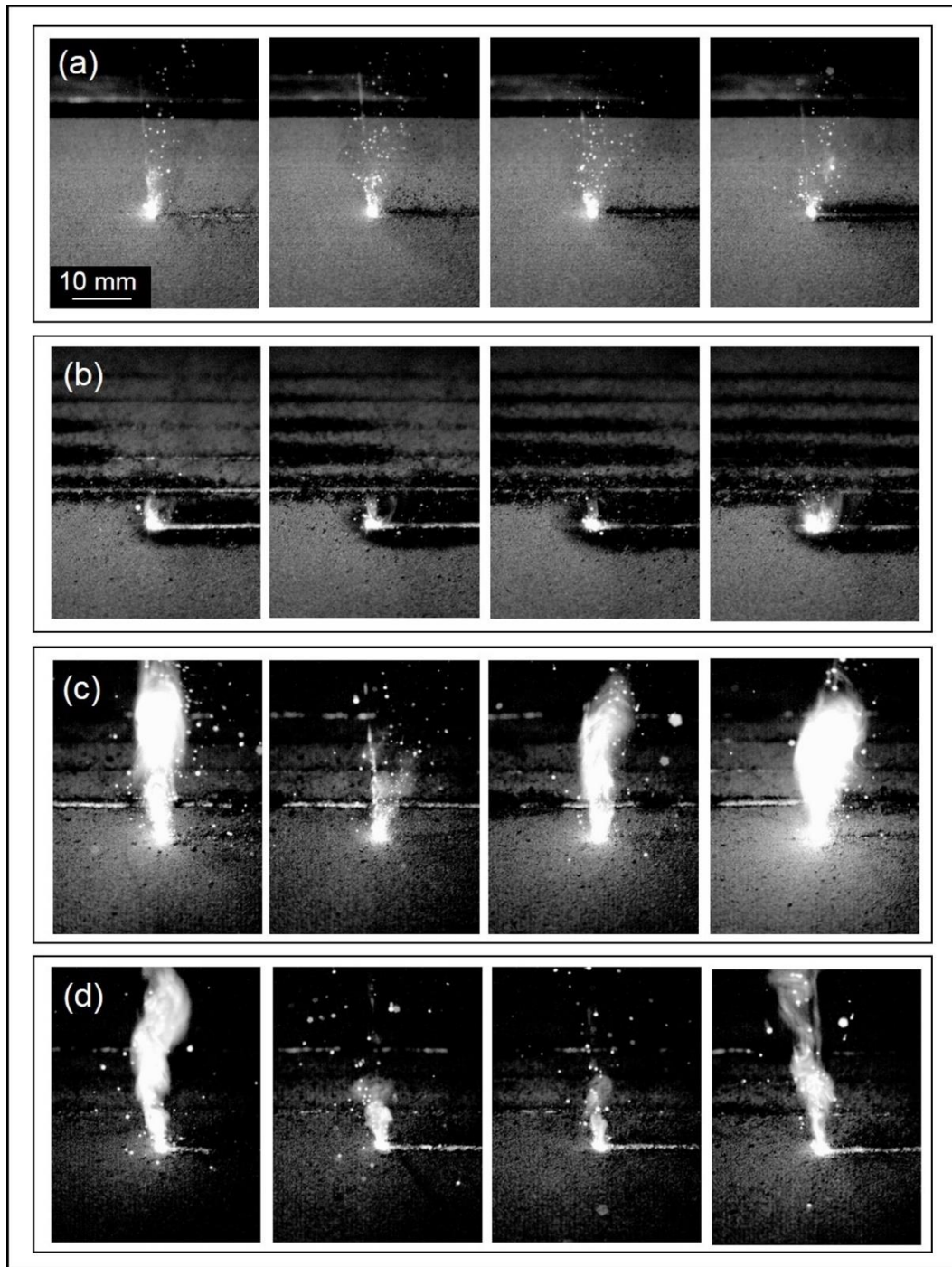


Figure 4-9. High speed imaging of powder melting under different global shielding conditions and interaction times. Helium global shielding (a) 0.35 ms and (b) 4 ms. Argon global shielding (c) 0.35 ms and (d) 4 ms. The time intervals between captions are 93 ms and 310 ms for interaction times of 0.35 ms and 4 ms respectively. Power density: 7100 kW/cm².

The combined effect of power density and interaction time (energy density) on penetration depth and bead width for powder melting under global helium atmosphere is shown in **Figure 4-10**. It is clear that penetration depth and bead width increase when the energy density is increased. Moreover, this is done in a repeatable and controlled way.

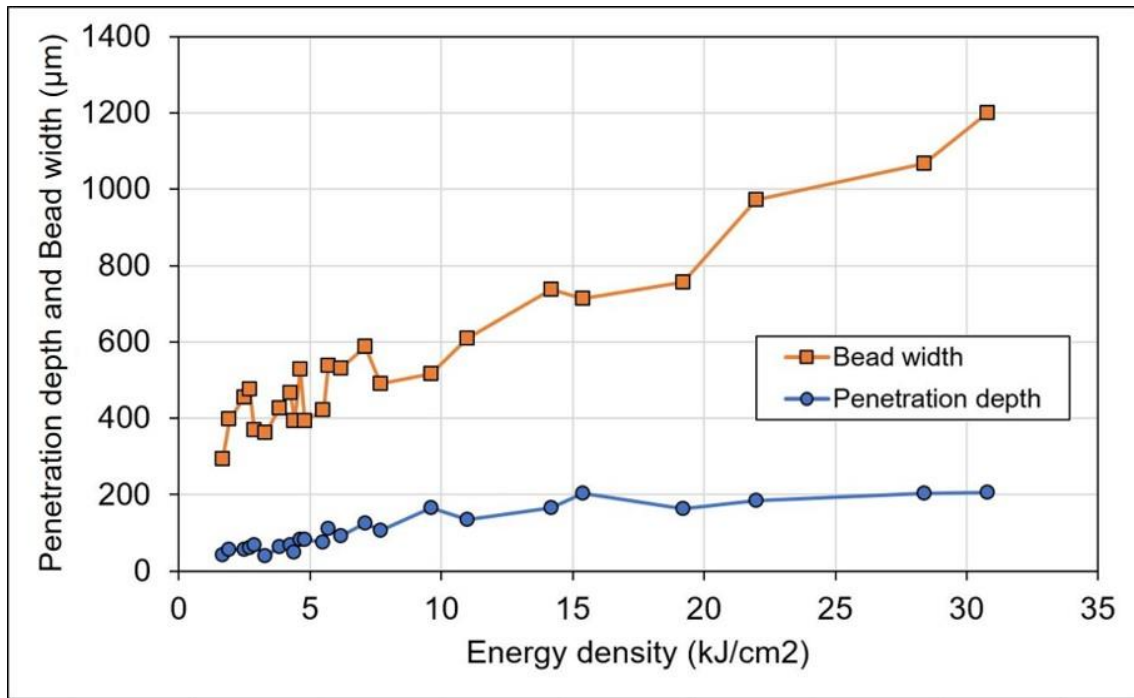


Figure 4-10. Effect of energy density on penetration depth and bead width. Powder melting under helium global shielding.

The effect of processing parameters on melt height is presented in **Figure 4-11a**, where it is shown that height also increases with increasing interaction time but it is not greatly influenced by power density changes. **Figure 4-11b**, compares the bead area measured from the extracted cross-sections as a function of interaction time and power density for both powder and solid materials. Since the bead area is the amount of material that undergoes melting during processing, this comparison gives a quantitative evaluation of what percentage of the laser energy is utilised by the powder and solid material for melting. For shorter interaction times (0.35 ms and 2 ms) the laser energy utilised by the powder and solid is similar. However, when the interaction time increases to 4 ms, powder has a higher melting efficiency as compared to solid.

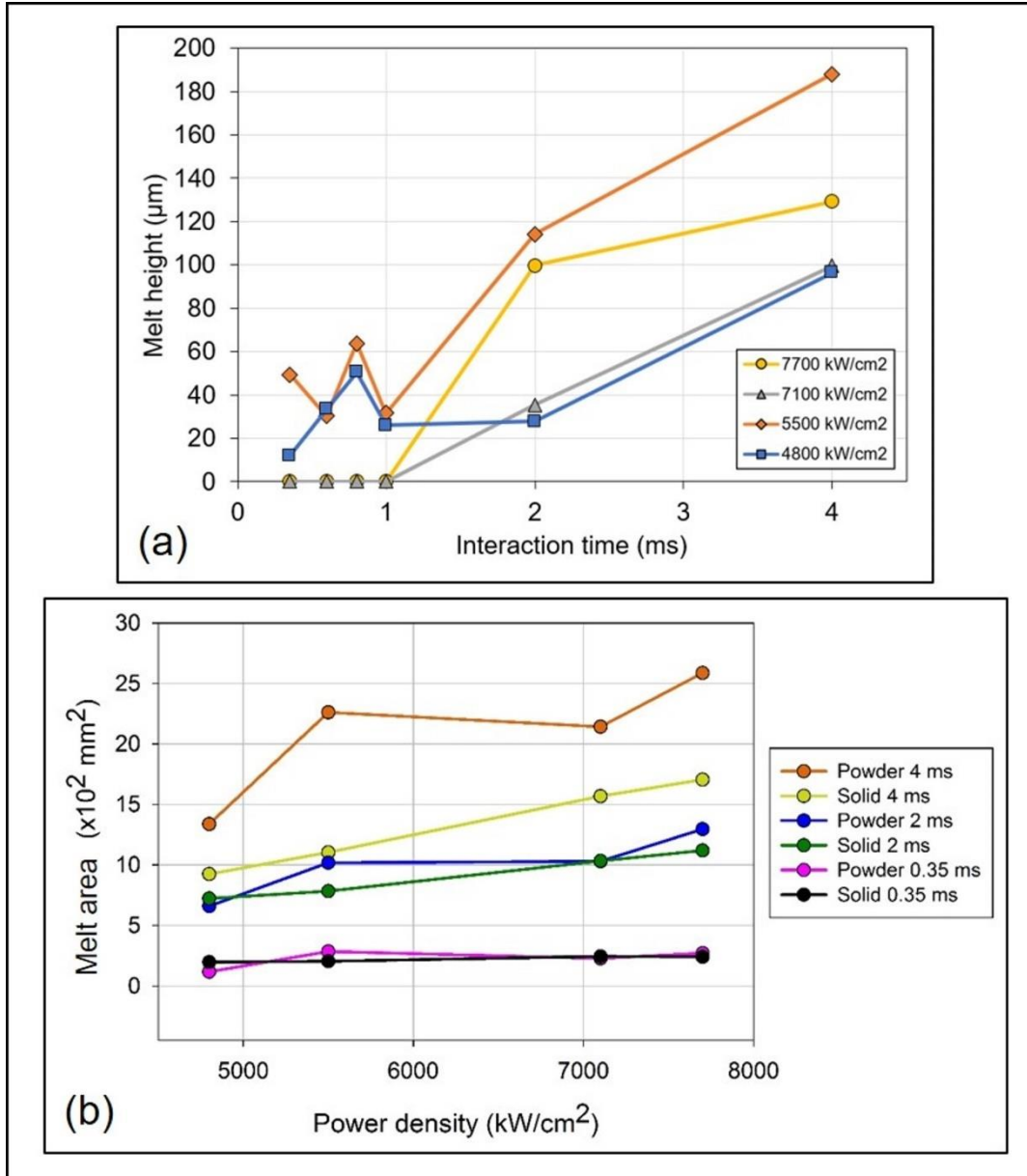


Figure 4-11. (a) Effect of power density and interaction time on melt height, powder melting. (b) Melt area as function of power density for powder and solid at different interaction times. Powder melting under helium global shielding.

The aspect ratio of all beads deposited under global argon and helium atmosphere and for solid and powder materials are summarised in **Figure 4-12**. The data is plotted as a function of energy density. Aspect ratios lower than 0.4 correspond to the conduction regime, while values between 0.4 and 0.6 are considered to be in a transition regime between conduction and keyhole. Values higher than 0.6 are characteristic of the keyhole regime [24]. These thresholds

have been marked on the plot as red horizontal lines as a reference. In argon, it is clear how more melt profiles are in the keyhole and transition regime. On the other hand, in helium, most profiles are in the conduction regime for solid melting while all profiles are in the conduction regime for powder melting.

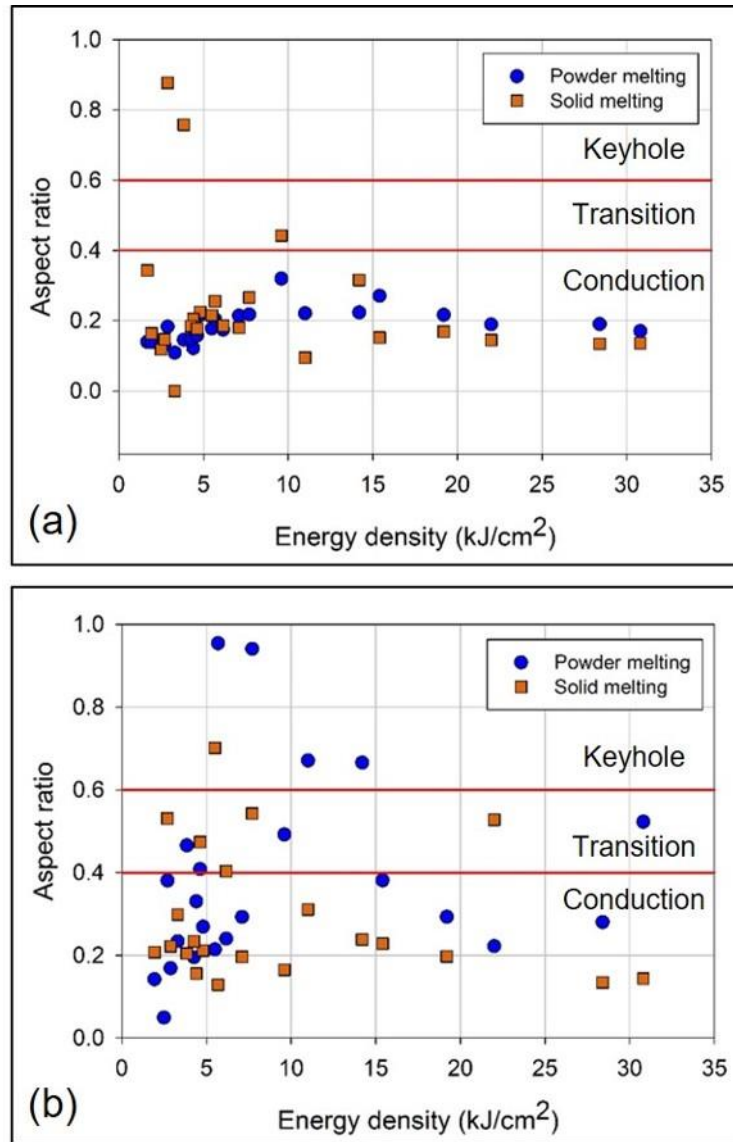


Figure 4-12. Aspect ratio as a function of energy density for powder and solid melting under (a) Helium global shielding and (b) Argon global shielding. Aspect ratio < 0.4, conduction. 0.4 < Aspect ratio < 0.6, transition. > 0.6, Keyhole.

4.4 Discussion.

4.4.1 Plasma plume fluctuations under argon global shielding.

Strong fluctuations on penetration depth and plasma plume characteristics were observed under an argon shielding atmosphere (**Figure 4-4** and **Figure 4-6**). The same behaviour was observed for both a single powder layer and solid substrate. Hence, the possibility that such fluctuations are caused by the presence of powder particles can be ruled out. Two important features can be identified for the plasma plume under this condition. First, the generated plasma plume is pulsed in character, and secondly, it reaches a high intensity for some time intervals. The pulsated characteristic of the plasma has been observed before for melting using a continuous wave laser beam. As reported by Mrna and Sarbort [25], this is due to the laser beam absorption by the plasma that fills the keyhole, which causes an increase in temperature and pressure and a further increase in the absorption itself. Once a critical limit is exceeded the plasma expands out of the keyhole generating a burst and the process repeats.

The plasma plume burst is accompanied by a change in melting regime that switches between keyhole, when a high intensity plasma is observed, to conduction when the plasma loses intensity (**Figure 4-5**). Heat conduction losses and laser beam-plasma interactions can be suggested as the underlying mechanism of this observation. As shown by Ayoola et al [26], when a smaller beam size is used, the transition window between conduction and keyhole becomes narrower as a consequence of an increased ratio of energy losses to the energy utilised as the laser beam size decreases. Hence, any attempt to increase the input energy to overcome these losses is likely to result in vaporisation and transition to a keyhole regime.

As summarised in the introductory section, significant changes in melting stability and bead geometry by using different shielding gases have not been observed before when laser sources with a wavelength of 1.064 μm are used. Hence, it would not be expected to find such significant changes in these two factors by changing shielding gas from argon to helium for the wavelength of the fibre laser used in this work. It can be suggested that this disagreement is due to the fact

that even though a very small percentage of the laser energy is being absorbed by the plasma plume for this wavelength, still the changes are enough to produce a fluctuation between conduction and keyhole. This is due to the fact that for this particular small beam size, even small changes in the input energy can generate a transition between melting modes due to the narrow operating window that exists under this particular condition [26]. An additional factor to consider for the laser beam-plasma plume interactions is the presence of refractive index gradients in the volume surrounding the processing point. Such gradients are formed due to the combination of heated gas, metal vapour and plasma, which are likely to contribute to further process instabilities such as focal shift and lateral laser spot wandering [27].

4.4.2 Global argon shielding with cross flow.

It has been shown that for the same range of parameters, an argon gas cross-flow helps to stabilise the melting regime (**Figure 4-7**). However, even though a more stable process is obtained under this shielding condition, some fluctuations and instabilities of the plasma plume could still be observed. As previously described, when argon is used as the shielding gas, a strong plasma plume forms, which interacts with the laser beam. The gas cross-flow has the ability to blow away and deflect the plasma plume which reduces the characteristic length of plasma through which the laser beam has to cross. Also, the fresh gas from the cross-flow supplies fresh argon and dilutes the plasma/plume requiring more energy for its ionisation. All these effects minimise the interaction between laser energy and plasma/plume and any focal shift or laser spot wandering that could take place due to the local refractive index gradients. It is also suggested that the inverse bremsstrahlung absorption of the plasma, which is a measure of the amount of laser radiation absorbed by the plasma, could be slightly modified under this condition and therefore the transmittance rate of the laser energy could marginally increase. This would contribute to a better utilisation of the laser energy during laser PBF. This behaviour was reported before by Xu et al [28] for laser welding, where it was shown that an increase in shielding gas flow rate led to lower plasma plume energy absorption and to higher transmittance rates when

an argon atmosphere was used. However, it should be mentioned that an effective cross-flow gas is difficult to set up experimentally, as it needs to be in an optimal and consistent position. If the cross-flow is too low with respect to the powder surface it will disturb and scatter the powder particles. On the other hand, if the cross flow is too far from the surface it will not have the desired stabilisation effect. The height and brightness of plasma plume were also observed to decrease with decreasing interaction time whilst using the gas cross flow. This could be due to the fact that further ionisation of the plasma plume cannot take place as it is constantly being replaced by a “fresh” plume, thus limiting its volume.

4.4.3 Melting characteristics under helium global shielding.

The instabilities observed during melting under argon atmosphere were suppressed when helium shielding was used instead of argon (**Figure 4-9**). In this case, the plasma plume did not show strong fluctuations in the form of strong bursts and its intensity and size were significantly lower, as compared to ones obtained in argon. Electron temperature and electron density, two important fundamental parameters to describe the state of a plasma plume, can be used to explain this behaviour. As reported by Xu et al [28], the electron temperature and density of the plasma plume in a helium atmosphere will be lower as compared to argon. This is due to the significantly higher ionization potential of helium (24.46 eV) in contrast to argon (15.68 eV). Therefore, a helium atmosphere can effectively prevent further ionisation of the plume, which translates into a smaller plasma that will cause less disruption in the laser-powder coupling. A comparison between powder melting in helium and argon (**Figure 4-4** and **Figure 4-8**) shows that not only the plasma eruptions are minimised under a helium atmosphere, but also that the melting regime is consistent and is predominantly in conduction mode (**Figure 4-12**). This supports the observation that fluctuations in the plasma plume behaviour are directly linked to fluctuations in the melting regime which produce very different melt pool geometries. These results demonstrate that control of the plasma plume during laser PBF is key to ensuring the stability of the process. Hence, the use of a gas cross-flow as a way to stabilise the melting was also explored.

The changes previously described in here, regarding melting stability and particularly the conduction-keyhole fluctuations as a function of shielding gas used for fibre laser, together with the small laser beam used, constitute some of the novel findings of this work as compared to previously reported results in the literature which discuss the role of argon and helium gas on laser welding. Hence, these results imply that the shielding gas combination used during fibre laser PBF is an important factor to consider if the melting behaviour wants to be predicted and controlled in order to increase the robustness of the process.

4.4.4 Correlation between bead geometry and processing parameters under helium global shielding.

For a helium atmosphere, as the energy density increases, both penetration and width also increase (**Figure 4-10**). As the interaction time gets longer, there is more time for the heat to transfer through the powder material and then by conduction into the substrate. This heat conduction is uniform in all directions in the solid substrate, resulting in hemi-spherical isotherms and melt profiles. However, in some cases, a small P/W aspect ratio of melt geometry can be identified, especially for longer interaction times (**Figure 4-8**), where the melt width can reach up to ten times the beam diameter used. According to Ayoola et al [26], the weld width in conduction melting is expected to be proportional to the beam diameter as the latter controls the size of the domain over which the heat is applied. Hence, it was found that beam sizes larger than 1 mm produce melt geometries of the same width size. In contrast, the small P/W ratios reported in this work suggest that for the small beam size used (100 μm), the bead profile is not only controlled by heat conduction, but also by an additional heat transfer mechanism. When a smaller beam is used, a higher localised laser heating (higher power density) is expected as compared to a larger beam. This produces higher temperature gradients on the surface of the melt pool. Such gradients generate strong surface-tension-driven shear forces (Marangoni effect) in the melt pool that widen the bead. Evidence that the geometry of the melt is being partially controlled by this effect is the wavy melt pool boundary that can be observed in some of the cross sections (**Figure 4-13**). When the liquid pool obtained is larger than the beam diameter used, heat transfer near the fusion

boundary becomes controlled by the liquid flow owing to Marangoni eddies [29]. Such flows produce two recirculation loops in the molten metal. The loop closer to the surface has very high velocities driven by the strong temperature gradient at this region. These loops then cause the liquid in the lower part along the melt centreline to recirculate in the opposite direction, thus creating a wavy fusion boundary [30].

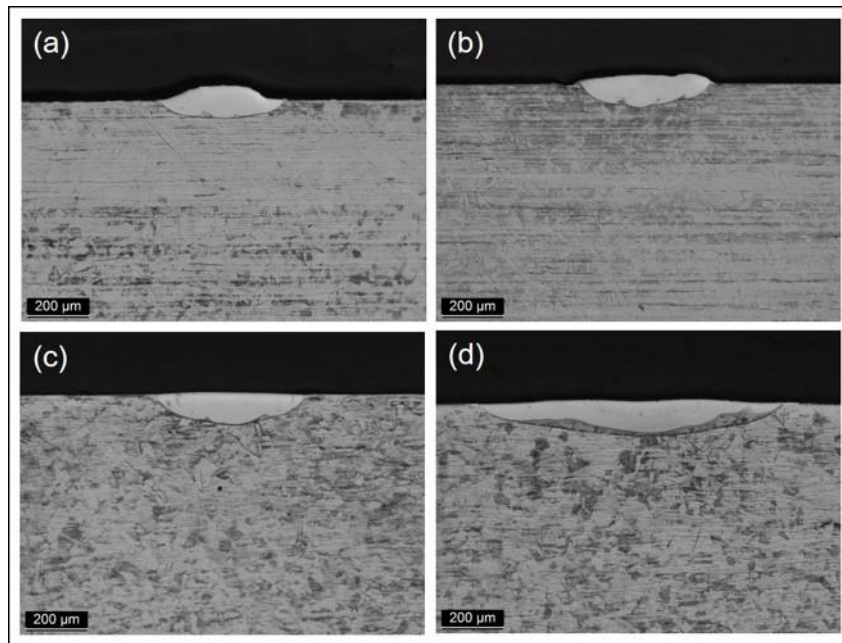


Figure 4-13 Bead profiles showing a wavy fusion boundary for both powder and solid substrate melting. Helium atmosphere. Power density 5500 kW/cm². (a) Interaction time: 0.35 ms (b) Interaction time: 1 ms (c) Interaction time: 0.8 ms (d) Interaction time: 2 ms.

Figure 4-14 shows the comparisons of the melt bead cross-sections between simulation results and experimental data. With various interaction times, the calculated bead shapes were consistent with the experimental data. Note that the calculated depths are slightly smaller than the measured data, especially for longer interaction times. This is probably because the free surface deformation caused by the Marangoni shear stress and the recoil pressure due to the evaporation has not been considered. However, in the context of this work, the model proves that strong Marangoni flow exists in melt pools achieved with this

small beam diameter and high power density and this flow expands the melting in the lateral direction beyond the extent of the beam diameter. **Figure 4-15** shows the distributions of temperature and velocity with an interaction time of 4 ms. When a high laser power density irradiates the surface of the substrate, the temperature at the centre point increases almost instantaneously to be around the boiling point of the metal (3375 K). Hence, as explained previously, a large temperature gradient is present in the melt pool, causing large Marangoni shear stress on the surface. The maximum speed of the transverse flow at the surface of the melt pool reaches up to 3.5 m/s for 4 ms. Thus, a larger width is achieved with longer interaction times within the range tested.

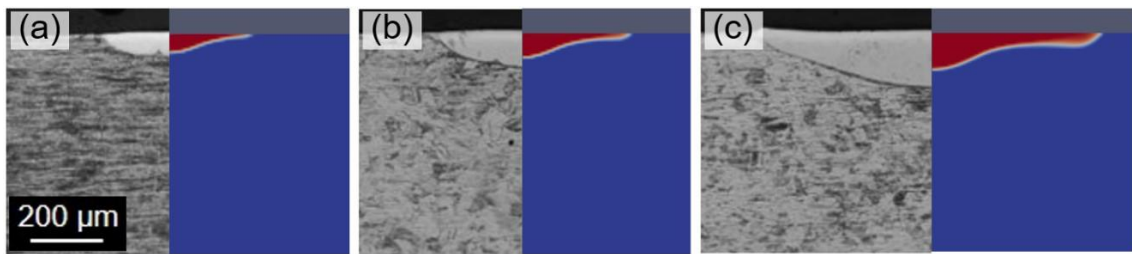


Figure 4-14. Comparisons of weld cross-sections of solid melting between simulation results and experimental data under different interactive times (a) 0.35 ms; (b) 0.8 ms; (c) 4 ms. Power density: 5500 kW/cm².

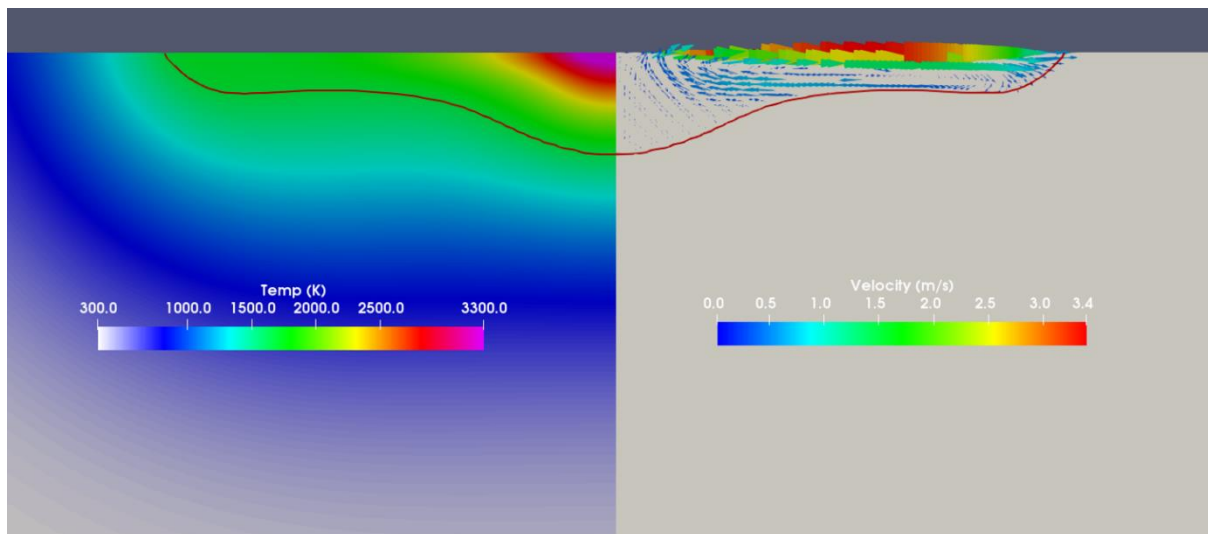


Figure 4-15. Distribution of the temperature and velocity of solid melting under the interaction time of 4 ms. Power density: 5500 kW/cm².

A closer look at **Figure 4-11a** reveals that no powder consolidation is obtained for power densities higher than 5500 kW/cm^2 and interaction times shorter than 1 ms. This is due to a combination of denudation of the powder bed and to high processing speeds that generate additional gas-driven powder particle ejection. For lower power densities and longer interaction times, the melt height increases. As interaction time increases the melt width also increases, improving the chance of the powder particles to be incorporated into the melt pool and increasing the height of the built. The maximum height obtained is around $200 \text{ }\mu\text{m}$ when a power density of 5500 kW/cm^2 and an interaction time of 4 ms were used. This value is lower than the powder layer thickness of $250 \text{ }\mu\text{m}$ used in this work. The observed difference is due to the elimination of voids between the powder particles and powder consolidation once the melting is performed. Similar laser energy utilization is experienced by the powder and the solid substrate for short interaction times (**Figure 4-11b**). In contrast, once the interaction time increases, powder melting shows higher energy utilization, which translates into a higher melting efficiency as compared to solid melting. A longer exposure time to the laser energy means that more time is allowed for absorption to take place. Additionally, due to high surface area of powder, laser energy absorption of the powder is higher as compared to the solid substrate. Since the process is predominantly in conduction mode no additional absorption of laser energy associated with the keyhole regime take place. It is shown in this work, that even though laser PBF benefits from high scanning speeds as a way of increasing build rates, using lower scan speeds (longer interaction time) leads to an improvement in the consolidated layer height and better utilization of the laser energy. Longer interaction times help to achieve higher powder consolidation and better laser energy utilisation.

4.5 Conclusions.

This work provides further insight into the effect of different shielding conditions on the melting behaviour and geometry of single powder layer tracks under different processing conditions. The following conclusions can be drawn:

- For powder and solid substrate, melting under an argon atmosphere leads to random fluctuations in melting mode (conduction-keyhole) and a high intensity plasma plume that causes melting instabilities and does not allow control of the bead profile.
- Controlling the plasma plume leads to a more stable melting as it minimises the laser beam-plasma plume interactions. Both local gas cross flow and helium shielding atmosphere proved to be effective ways of mitigating such instabilities.
- Under the helium atmosphere, the strong fluctuations in melting mode and plasma intensity were no longer observed and most achieved beads exhibited profile characteristics of conduction regime. Under this condition, better control of the bead profile was achieved in contrast to argon.
- For melting under helium shielding, penetration and bead width are controlled by energy density.
- Bead width was found to be up to ten times the beam diameter used. A wavy fusion boundary in the analysed profiles and two-dimensional numerical simulations suggest that the width is controlled by strong surface tension-driven Marangoni flows under some conditions.

4.6 References.

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5 Wire + Arc Additive Manufacture of 17-4 PH stainless steel: Effect of different processing conditions on microstructure, hardness, and tensile strength.

This chapter is based on the following publication.

A. Caballero, J. Ding, S. Ganguly, S. Williams. *Wire + Arc Additive Manufacture of 17-4 PH stainless steel: Effect of different processing conditions on microstructure, hardness, and tensile strength*. Journal of Materials Processing Technology. 268 (2019) 54-62. doi: <https://doi.org/10.1016/j.jmatprotec.2019.01.007>.

The second step of this research was to study the role of different shielding conditions in arc-based AM. The influence of different shielding conditions on the developed microstructure was investigated for WAAM deposition of 17-4PH. As part of the research approach implemented in this work, it was also investigated the criticality of different thermal cycles over the microstructure evolution and mechanical properties of the deposit. Evidence is provided showing that shielding gas used and different deposition parameters (different deposition strategies) have little influence on the mechanical properties and the final properties can be controlled effectively by applying post-deposition heat treatment.

Abstract: Wire + Arc Additive Manufacture (WAAM) is receiving increasing attention as it offers a way to fabricate meter scale parts, with relatively low capital cost, lower material wastage and logistical advantages. A wide range of metallic alloys could be manufactured using this process. Martensitic grade precipitation-hardening stainless steel 17-4 PH offers an excellent combination of high strength and corrosion resistance. Hence, it is important to investigate the behaviour of this alloy in WAAM. In the present work, the effect of different process variables such as shielding gas, deposition path and post-fabrication heat treatment, on microstructure and mechanical properties were studied. A number of specimens were manufactured by WAAM using the Fronius Cold Metal Transfer (CMT) process under different controlled processing conditions. These specimens were subsequently characterized by optical and electron microscopy and mechanical properties in terms of tensile strength and hardness. It was found that using

shielding gases that result in higher heat input reduces the amount of retained austenite in the as-deposited microstructure. It has been demonstrated that the required tensile properties can be achieved by applying post-deposition heat treatment. However, it is suggested that direct ageing in as deposited condition resulted in the formation of harmful intermetallic phases which embrittles the deposit.

Keywords: Additive Manufacture; WAAM; Retained Austenite; Stainless Steel; 17-4 PH.

5.1 Introduction.

Additive manufacturing has several advantages as compared to traditional manufacturing processes, including the potential reduction of costs and lead times and the possibility to deposit shaped components [1]. Depending on the material feedstock, AM systems can be classified as powder bed, powder feed or wire feed systems [2]. The latter has experienced increasing interest through the wire + arc additive manufacture (WAAM) process, where an electric arc is used as the heat source, in combination with metallic drawn wire as feedstock and a manipulation system e.g. robot or multi-axis tables in order to fabricate near net shape components through layer by layer deposition. The main benefits of WAAM over traditional manufacturing processes include the capability of building medium to large-scale components at relatively high deposition rates, reduction in material waste and low capital and feedstock costs. Ti-6Al-4V, aluminium, steel, copper, and nickel alloys have been successfully deposited by WAAM [3]. Precipitation-hardened martensitic stainless steel, 17-4 PH, is a good candidate for WAAM as it could provide a good combination of strength and corrosion resistance which are ideal for the intended severe service conditions such components are subjected to. Additionally, it provides the possibility of tailoring mechanical properties through controlled heat treatment. High strength in this material is obtained by the precipitation of dispersed sub-microscopic Cu-rich phases inside the martensitic matrix during ageing [4].

WAAM deposition of 17-4 PH has only been covered by Martina et al [5]. However, this work focuses more on the feasibility of achieving high deposition

rates during manufacturing. Very few details are provided regarding the microstructure, mechanical properties or post-manufacturing heat treatments to be applied in order to obtain satisfactory properties. The rest of the previous investigations on additive manufacture of 17-4 PH stainless steel are mainly based on laser + powder processing, where 3D components are manufactured by layer-by-layer melting of a pre-placed metallic powder bed using a laser beam. Some of these works have focused on the microstructure and mechanical properties of selective laser melting (SLM) of 17-4 PH stainless steel. LeBrun et al [6] investigated the influence of thermal processing after SLM and its effect on retained austenite and mechanical properties. They showed that a solution heat treatment is necessary after fabrication in order to achieve satisfactory properties after ageing, mainly due to high percentages of retained austenite in the as-fabricated condition. Moreover, they determined an increase in work hardening rates during tensile testing of as-fabricated specimens as a consequence of the stress-induced transformation of the retained austenite to martensite. Facchini et al [7] found similar results where 17-4 PH samples produced by SLM exhibited exceptional work hardening as a consequence of the same solid-state transformation. However, in contrast to LeBrun et al [6], they were not able to achieve the required tensile properties after thermal processing of additively built 17-4 PH. This is probably due to the fact that Facchini et al [7] identified 72% of austenite in the as-fabricated condition as compared to 36% found by LeBrun et al [6]. Ageing response of austenite is not satisfactory due to its higher solubility for Cu-precipitates [8]. Therefore, strengthening by ageing of this alloy is limited by higher percentages of retained austenite. The unusual high volume percentages of this metastable phase reported in the aforementioned literature are seen to be a consequence of mechanical stabilisation due to thermomechanical residual stresses accumulated during the repetitive solidification and cooling down cycles experienced by the samples during SLM processing. Despite the tensile test analysis carried out by the previously mentioned works, none of them has considered the comparison of tensile properties both in parallel and perpendicular direction, with respect to the building direction. Nevertheless, additional mechanical properties characterization,

including fatigue resistance and hardness, have been performed on selective laser melted 17-4 PH.

Comprehensive hardness maps were presented by Rashid et al [9] for two different SLM scan strategies, single and double melting of each layer. It was found that the hardness values for the double melted samples were higher as less percentage of retained austenite was found for this condition, 485 HV and 14% respectively in contrast to 365 HV with 33% of retained austenite observed in single melted layer samples. Cheruvathur et al [10] also reported hardness values variation from 258 HV, in the as-fabricated condition, up to 318 HV after solutionizing heat treatment. LeBrun et al [6] measured 333 HV and 330 HV for the as fabricated and solution treated condition correspondingly. We can suggest that the differences in hardness values described by various authors are related to the use of a wide range of different SLM process parameters during fabrication, such as scanning speed, powder layer thickness, laser power, laser spot size and hatch distance. Each specific combination of these variables will produce unique cooling rates and thermal cycles that can create very dissimilar microstructural features. Another factor that could cause a difference in hardness and percentages of retained austenite is changes in chemical composition. Depending in the process parameters used, local compositional gradients could be developed due to microsegregation, dictating changes in the solutionizing temperature of the material and its reaction to different thermal cycles. Yadollahi et al [11] went a step further with the mechanical characterization of SLM 17-4 PH and tested the effect of building orientation and post-fabrication heat treatment on fatigue behavior. Finding a higher fatigue strength of horizontally built specimens due to the orientation of deposited layers and defects with respect to the loading axis. As described in this section, tensile properties, fatigue resistance and hardness measurements have been performed on SLM 17-4 PH samples, proving that the percentages of retained austenite can have an important effect on final mechanical properties and heat treatment response. Hence, investigation of this retained phase and its quantification have been one of the main focus of previous research. Due to some similarities shared between

fusion welding and AM, it is also worth exploring the state of this field regarding 17-4 PH, specifically arc based welding, which principles are similar to WAAM.

Microstructure and hardness of the weld metal and heat affected zone (HAZ) of 17-4 PH have been characterized before for arc-based welding. Ziewiec and Tasak [12] reported that the weld metal after gas tungsten arc welding (GTAW) is formed by lath martensite with interdendritic δ ferrite. However, more attention has been put in the characteristics of the HAZ as it is known that solid state heating of this alloy can cause changes in the microstructure. Including precipitates dissolution and reverse transformation from martensite to austenite, both having negative effects on mechanical properties. For this reason, Bhaduri and Venkadesan [13] studied in detail the microstructure and hardness of the HAZ for different weld heat inputs and different starting conditions. They found that, regardless of the heat input used after welding of 17-4 PH in condition A and H900, a significant drop in hardness is experienced as compared to the base metal. They verified that indeed austenite is reformed in the HAZ together with the solutionisation of existing precipitates. Additionally, they stated that further contributing factors to the softening of the HAZ are the overaging of the martensitic matrix and the tempering of the martensite laths. Deng et al. [14] reported similar results after performing plasma-transferred arc welding of 17-4 PH, coming to the same conclusions that softening of the HAZ is caused by the aforementioned mechanisms. It is for this reason that a common approach to restore the mechanical properties after welding is to perform post weld heat treatment (PWHT).

The effect of different standardized heat treatments after welding of 17-4 PH on mechanical properties and microstructure have been investigated in detail. For example, Das et al [15] and Prabhakar et al [16] demonstrated that satisfactory tensile properties can be restored by applying the appropriate heat treatment after welding. However, both of these works focused on single pass welding and do not provide any insight if the same can be achieved in the case of multi pass welding. As described in the previous section, reheating can have detrimental effects in 17-4 PH microstructure. Hence, the effect of cyclic heating and its

accumulated effect needs to be taken in consideration, especially if the knowledge wants to be transferred to a process such as WAAM. From the available literature, only the work of Bhaduri et al [17] covers the effect of PWHT on multi pass welding of 17-4 PH. They tested the effect of several heat treatments combinations including the aging of “as welded” material with and without a preliminary solution treatment (ST). It was found that if 17-4 PH is to be used in the H900 condition for practical applications, then a preliminary ST before aging is necessary to achieve satisfactory properties. They also found that applying a ST before aging reduces the hardness variations, suggesting that a more homogenous microstructure is obtained. Even though these results are useful for the understanding of 17-4 PH WAAM, it must be highlighted that a double V-grooved joint geometry with an effective welding thickness of only 13 mm was used in their work. Hence, it was not taken in consideration the further evolution of the microstructure when a higher number of passes (layers) are deposited. As reported by Zhao et al [18], the last deposited layers of Ti-6Al-4V manufactured by WAAM have a different microstructure as compared to previous layers, due to the incomplete thermal cycles experienced by this section. This region can be as large as 10-12 mm for Ti-6Al-4V and a comparable behaviour can be expected for 17-4 PH due to its similar thermal conductivity with titanium. This means that Bhaduri et al [17] findings may not be of much use to unveil the behaviour of WAAM 17-4 PH, as they only cover a section of the actual microstructure that it might develop during further deposition of a higher number of layers. Multi-pass welding of 17-4 PH was also covered by Hamlin [19]. However, only the effect of two welding passes on microstructure and hardness were described, not being enough to provide any useful insight of WAAM deposition of 17-4 PH.

Regardless of the efforts done to characterise additively manufactured 17-4 PH components, all current research focuses mainly on SLM. Additionally, research done in welding and the effects of PWHT on microstructure and mechanical properties, limits only to a few welding passes and do not represent the actual thermal conditions inherent to WAAM. In this paper, it is describe in detail the effect of different processing conditions and post depositon heat treatments, of

WAAM manufactured 17-4 PH components, on microstructure, hardness, and tensile strength.

5.2 Experimental procedure.

Samples in this work were deposited by Fronius cold metal transfer (CMT) process, using a travel speed (TS) of 6.2 mm/sec and a wire feed speed (WFS) of 6 m/min which gives a WFS to TS ratio of about 16. The same approach as the one described by Ayarkwa et al [20] was used to determine these suitable deposition parameters. Commercial 17-4 PH welding wire of 1.2 mm diameter was used. **Table 5-1** shows the chemical composition. Samples were deposited over 12 mm thick 304 austenitic stainless steel substrate.

Table 5-1. Chemical composition of 17-4 PH welding wire used.

Element	C	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	F e
Percentage (wt.%)	0.024	16.44	3.53	0.56	0.220	0.15	4.74	0.020	0.005	0.50	bal

Three different deposition strategies were investigated in the presented work: single pass deposition, oscillated and parallel pass (**Figure 5-1**). For a single pass, each layer is formed by a single bead of deposited molten metal. In the oscillated path, the torch moves with a specific oscillation width to form wider layers. Parallel pass consists of a sequence of single beads deposited next to each other in order to form each layer, wider widths can also be achieved with this strategy. Different deposition strategies are experimented with as they will induce different thermal cycles in the deposited metal due to dissimilar thermal masses and heat accumulation.

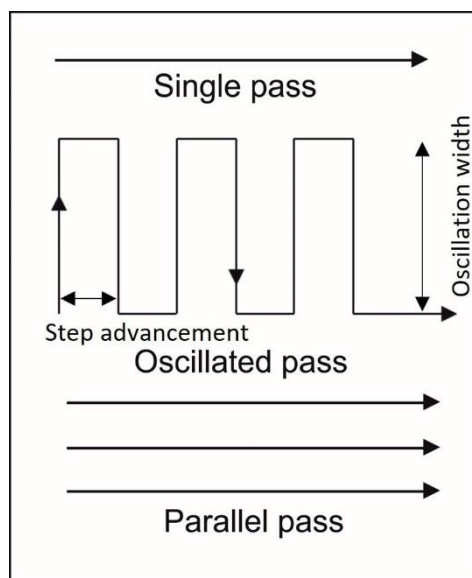


Figure 5-1. Different deposition strategies used in this work.

5.2.1 Shielding gas assessment.

Two different tailored shielding gas compositions were experimented during deposition of two single pass samples. In this text, they are referred to as shielding gas 1 (SG1) and shielding gas 2 (SG2). SG1 was made of 38% He and 2% CO₂ in argon. While SG2 was made of 2.5% CO₂ in argon. Samples were deposited inside a small argon filled environmental chamber to prevent any undue oxygen pick up of the deposited metal which would change the characteristics of the deposited bead. This allowed the study of the direct effect of the shielding gas on the microstructure of the deposited samples. Samples were 6 mm x 19 mm x 190 mm long and formed by 10 layers. The experimental set up is shown in **Figure 5-2**.

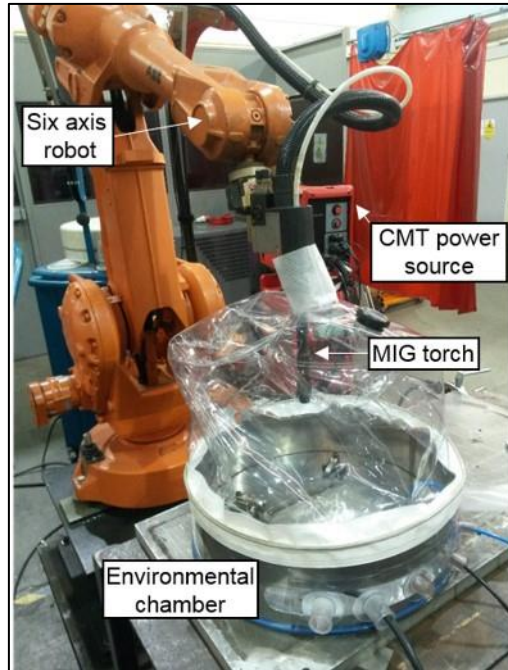


Figure 5-2. Experimental set up for the shielding gas assessment.

Electron backscatter diffraction (EBSD) pattern analysis has been carried out on these two samples with the purpose of identification and determination of different phase fraction distribution. The EBSD scan was focused near the middle region in the cross section of each sample and three different fields were analyzed.

5.2.2 Effect of different heat treatments conditions on different shielding gas and deposition strategies.

A series of heat treatments were performed on samples deposited using different deposition strategies. Shielding gas compositions, SG1 and SG2, were used to build specimens with both the oscillation and parallel deposition strategies. Samples dimensions are shown in **Figure 5-3**. Subsequently, 8 mm thick cross-sections perpendicular to the deposition direction were taken from each sample in order to apply the different heat treatments. Samples underwent standardised solution treatment (1040 °C for 30 minutes) and H900 ageing treatment (480 °C for 1h), an electric air furnace was used for this purpose. Four different conditions including as-deposited samples, were characterised as follows; as deposited (AD), as deposited plus solution treatment only (AD+ST), as deposited plus H900 ageing treatment (AD+H900) and as deposited followed by solution treatment

and H900 ageing (ST+H900). **Table 5-2** summarises the different deposition strategies adopted and the heat treatment conditions done. The aim of performing direct ageing on AD condition was to assess if required properties could be achieved without completing the ST step. Hardness measurements were performed as a function of the number of deposited layers (sample height).

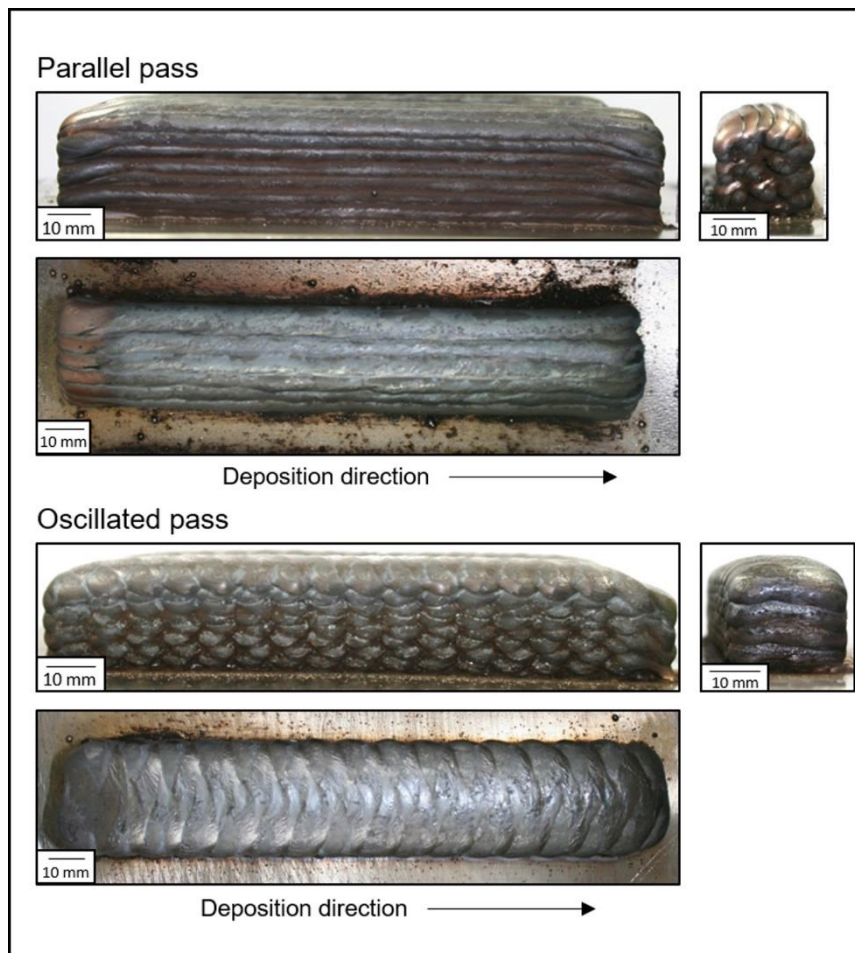


Figure 5-3. Dimensions of parallel and oscillated pass samples deposited to evaluate the effect of different heat treatments on samples built with different shielding gases and deposition paths.

Table 5-2. Experimental matrix of the different heat treatments performed.

Deposition Strategy	Shielding Gas	Heat treatment
Oscillated pass	SG1	AD
		ST
		AD+H900
		ST+H900
	SG2	AD
		ST
		AD+H900
		ST+H900
Parallel pass	SG1	AD
		ST
		AD+H900
		ST+H900
	SG2	AD
		ST
		AD+H900
		ST+H900

5.2.3 Effect of H900 ageing on tensile properties.

The response of the microstructure to different heat treatments and thereby on mechanical properties were investigated on as-deposited specimens. The same

four different conditions described in the previous section were studied on single pass deposited specimens to understand its effect on mechanical strength. Cross sections were extracted as indicated in **Figure 5-4a** along plane AB for metallographic analysis. Microstructural characterisation was performed in the middle section of plane AB. The mechanical anisotropy was studied by mechanical testing in both the horizontal and vertical directions of the single pass deposits (**Figure 5-4b**). Three coupons per condition were tested to determine the variation and they were machined from within the bulk of the samples. Coupon dimension was selected in accordance with the BS EN 2002-1: 2005 [21] and is shown in **Figure 5-4c**. Tensile testing was carried out using an electromechanical Instron 5500R frame with a load cell of 100 KN and a strain rate of 0.2 mm/min. For the purpose of this study, mechanical properties stated in ASTM A564/A564M-02a [22] standard were used as reference. Fractographic analysis was also carried out using a Philips XL-30 SFEG scanning electron microscope (SEM).

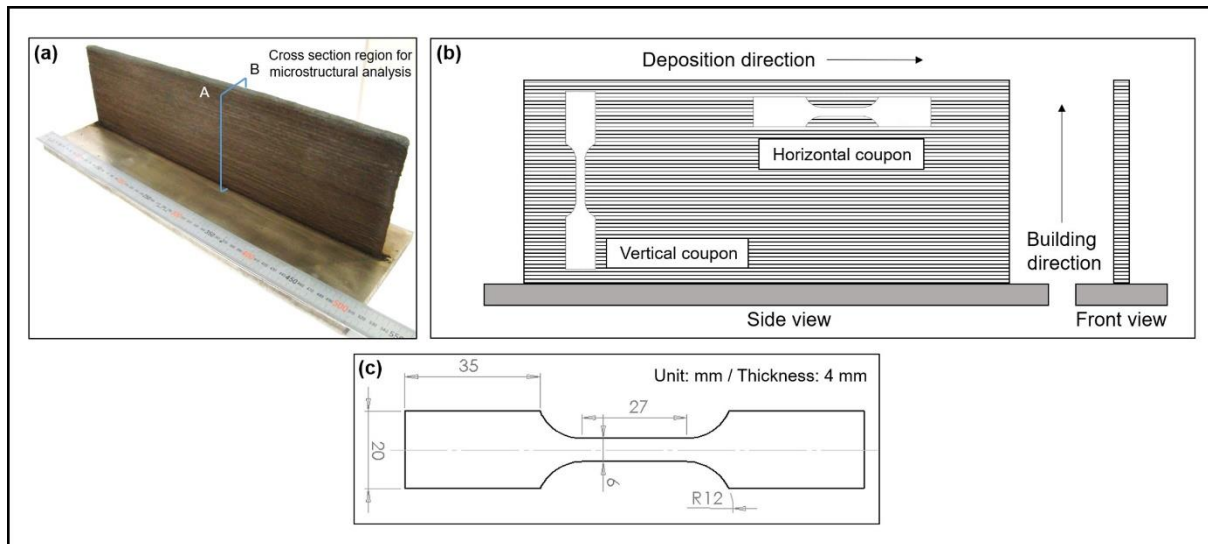


Figure 5-4. (a) Sample built for tensile testing, location and direction for microstructural analysis is shown; (b) Simplified diagram showing directions of tensile coupons relative to deposition direction; (c) Geometry of the uniaxial tensile specimens.

5.2.4 Samples processing.

For metallographic characterization, samples were ground using abrasive papers with grit from 120 to 2500 and polished using 6 μm and 3 μm diamond suspension, followed by final polishing with 0.5 μm colloidal silica. Kalling's 2 etchant (cupric chloride, hydrochloric acid and ethanol) was used to reveal the microstructure. Additionally, Vickers hardness measurements were performed according to BS EN ISO 6507-1 [23] using a load of 10 Kgs.

5.3 Results.

5.3.1 Microstructure examined by Optical Microscopy (OM) and EBSD.

Micrographs of WAAM samples built for tensile testing in the AD condition and after ST plus H900 ageing are shown in Figure 5-5. The AD condition is characterized by a dendritic microstructure with the presence of interdendritic δ -ferrite in a martensitic matrix (**Figure 5-5a**). A lower magnification field of a cross-section, perpendicular to the deposition direction, taken from the sample manufactured for tensile testing (**Figure 5-5b**), reveal a columnar microstructure orientated perpendicular to the building direction. In the ST and aged condition, the microstructure is mainly formed by tempered Martensite; δ -ferrite or the columnar features are no longer seen (**Figure 5-5c**).

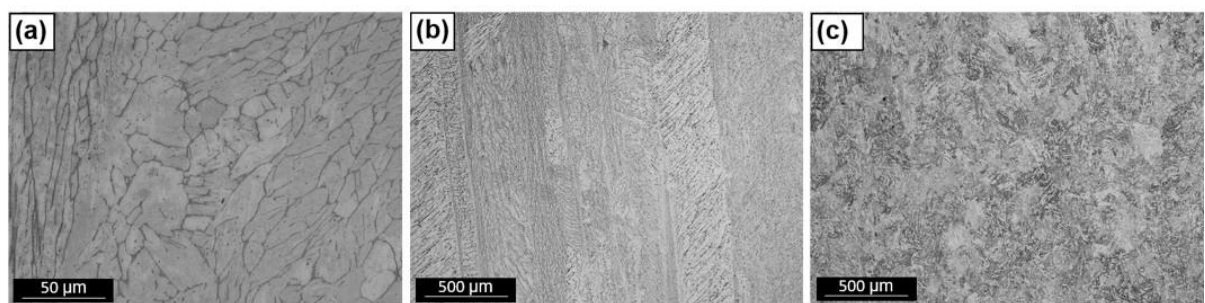


Figure 5-5. Microstructure: (a) As-deposited condition of sample manufactured with SG1; (b) Sample used for tensile testing, AD + H900 condition; (c) Sample used for tensile testing, ST+H900 condition.

Figure 5-6 illustrates the EBSD phase mapping results for samples manufactured using two different shielding gases (section 5.2.1). For the sample built using

SG2, a higher percentage of retained austenite was measured (0.85 %, area percentage) as compared to sample built using SG1 (0.12 %, area percentage). Images were processed to highlight the retained austenite (black/white contrast images on the right).

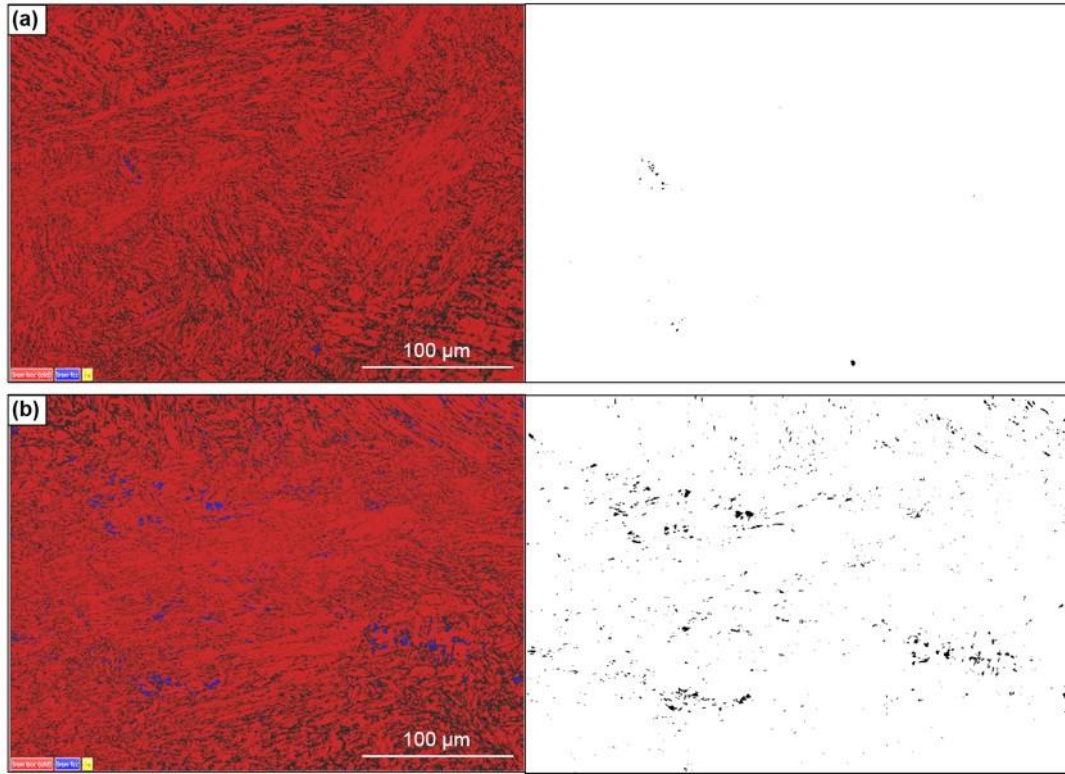


Figure 5-6. EBSD phase mapping for samples manufacture with SG1 (a); and SG2 (b). Showing BCC/Martensite and FCC/Austenite in red and blue respectively. Images on the right represent a high contrast version between the two main phases identified.

5.3.2 Effect of different heat treatments conditions on different shielding gas and deposition strategies.

Vickers hardness as a function of the sample height for each deposition strategy is presented in **Figure 5-7**. For the deposit produced by oscillation of the tool path (**Figure 5-7a**), it can be observed that the highest hardness corresponds to H900 ageing. The minimum and maximum values obtained for this treatment are 408 and 448 HV30 respectively. According to ASTM A564, minimum hardness value has to be 396 HV for condition H900. Hence, both AD+H900 and ST+H900 comply with the hardness requirements. Solution treated samples without any

further ageing show lower hardness in comparison with the AD state. Parallel deposition strategy samples (**Figure 5-7b**) also comply with the required hardness values and the same behaviour previously described can be observed. For both strategies, hardness does not change significantly as a function of the height (number of deposited layers).

The difference in hardness values by changing shielding gas is more significant for the oscillated strategy as compared to the parallel, particularly for H900 treatment. After solution treatment, the changes in hardness by using different shielding gases is minor. In the case of the parallel deposition, solution treating produces higher hardness for SG2 as compared to SG1.

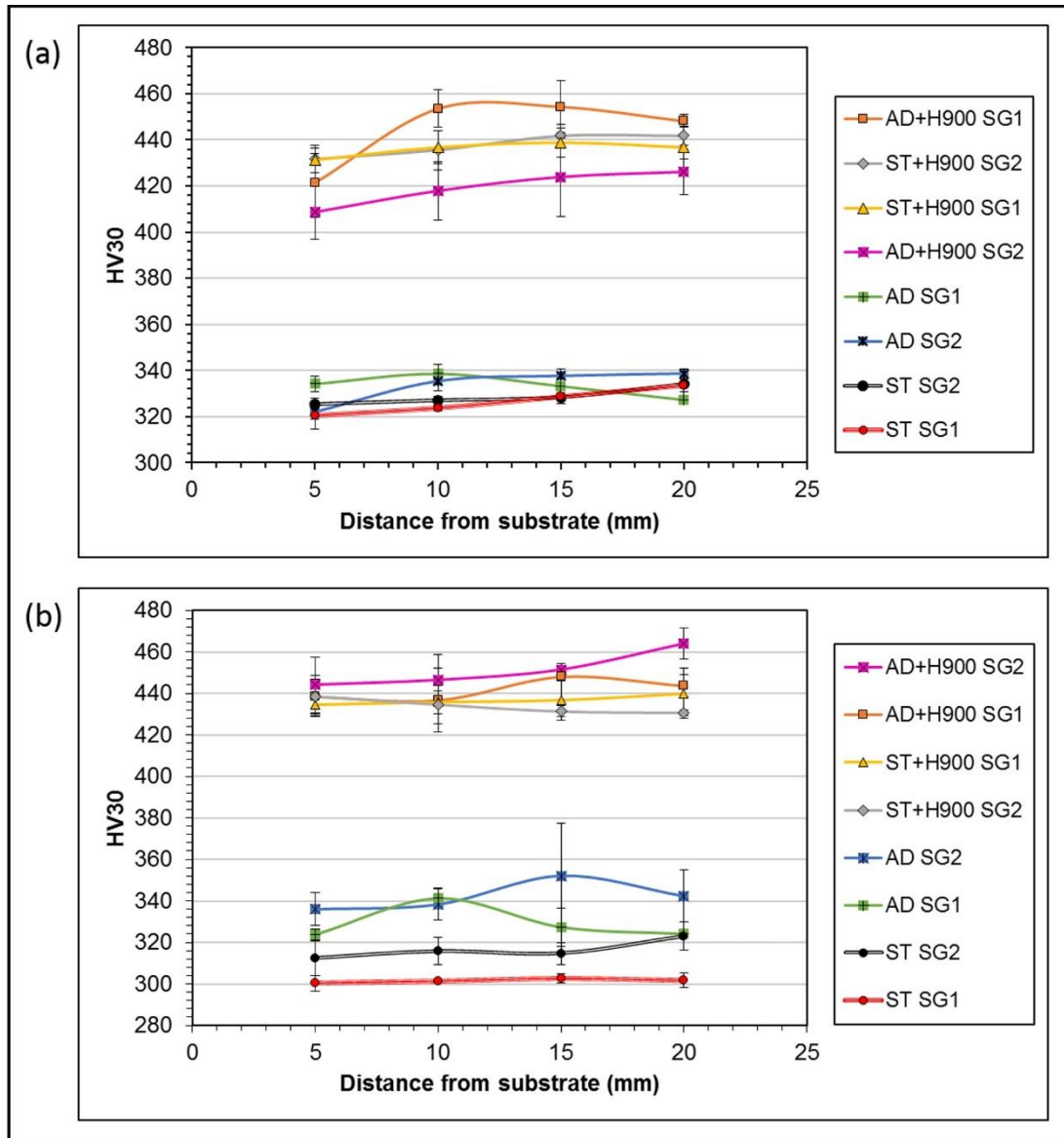


Figure 5-7. Hardness as a function of sample height (number of deposited layers). (a) Oscillated pass deposition strategy; (b) Parallel pass deposition strategy.

A hardness comparison between both deposition strategies with ageing treatment applied without prior solution treatment is plotted together in **Figure 5-8a**. For AD+H900 SG1 hardness values are not significantly different between oscillated and parallel passes; especially for distances of 15 and 20 mm from the substrate. There is a more significant gap amongst deposition strategies for the same AD+H900 condition built with SG2. A maximum value of 426 HV30 is observed for the oscillated pass, while 464 HV30 is measured as the maximum

for the parallel strategy. **Figure 5-8b** shows the hardness values after ST and subsequent ageing; it is evident from the plot that, for all combination of deposition strategies and shielding gases, hardness does not change in any significant way for each ageing treatment. This is, applying ST before ageing produces similar values of hardness for all the different process condition used, being dependent only on the subsequent ageing applied.

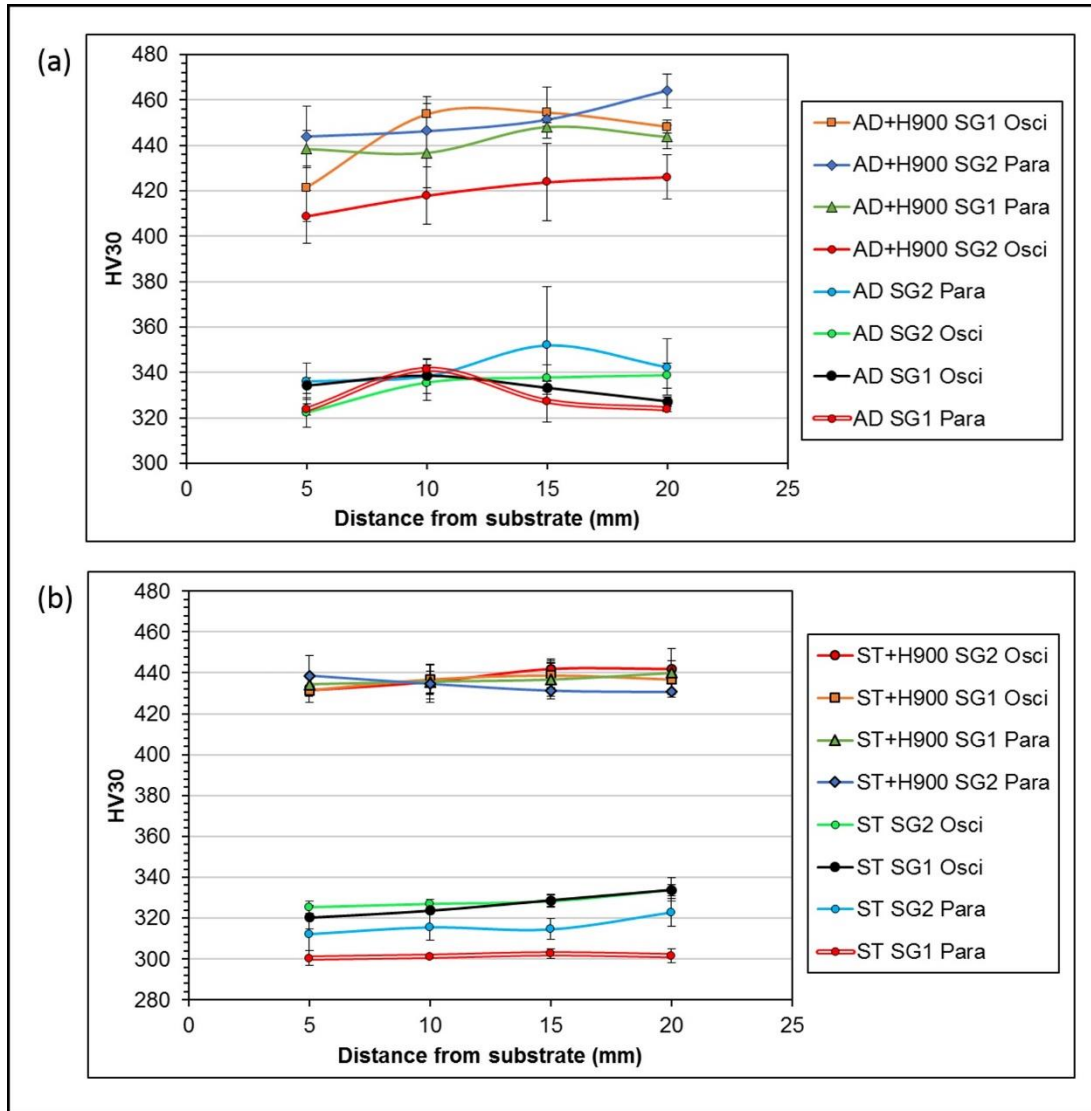


Figure 5-8. Hardness as a function of sample height. (a) Comparison between oscillated and parallel strategy with and without ageing in AD condition; (b) Comparison between oscillated and parallel strategy in ST condition with and without ageing treatment.

5.3.3 Effect of H900 ageing on tensile properties.

Table 5-3 summarises the results obtained from tensile testing. Only the samples with solution treatment and H900 ageing comply with the requirements of the ASTM A 564/A 564M-02a [22] standard for age hardened 17-4 PH (PS: 1170 MPa, UTS: 1310 MPa and 10% elongation). These samples give the highest PS at 1229 MPa, the highest UTS at 1352 MPa and the highest elongation of 13.8%. Solution treating the AD samples, without aging, only gives a marginal increase in tensile properties as compared to the AD condition. Direct H900 ageing of the AD condition produces an increase in PS and UTS as compare to AD and AD+ST samples. However, elongation percentage decreased significantly from 12% to 7%.

Table 5-3. Tensile properties results for different thermal processing conditions. Average and direction-specific results. Single pass deposition strategy using SG1.

Condition	Sample direction	PS (MPa)	Std dev	UTS (MPa)	Std dev	Elongation %	Std dev
AD	Average	790	73	994	39	11.9	0.6
	Vertical	738	30	979	13	12.2	0.7
	Horizontal	842	65	1009	55	11.6	0.3
AD+ST	Average	821	17	1003	6	12.6	0.4
	Vertical	827	4	1006	6	12.4	0.4
	Horizontal	815	24	1000	5	12.8	0.2
AD+H900	Average	1099	57	1208	95	7.3	1.2
	Vertical	1059	9	1124	5	6.5	0.3
	Horizontal	1140	57	1293	32	8.2	1.3
ST+H900	Average	1229	31	1352	8	13.8	0.9

	Vertical	1234	33	1351	11	13.8	0.5
	Horizontal	1225	36	1353	6	13.8	1.4

Within each condition, it does not seem to be a significant difference between properties and orientation. In order to assess this, the p-values of the t-student test were calculated. Anisotropy was only observed ($p\text{-value} < 0.05$) in the case of the UTS values for the AD + H900 condition.

Fracture morphologies obtained by SEM of vertically orientated tensile coupons, with respect to the deposition direction, are shown in **Figure 5-9a**. Tension-induced fracture morphology was dominated by round dimples in the case of the ST + H900 condition. For AD + H900 condition, dimples are identified, together with some localized regions where flat facets are observed, suggesting an overall inhomogeneity in the microstructure resulting in lower overall plasticity as compared to the ST + H900 condition (**Figure 5-9b and c**).

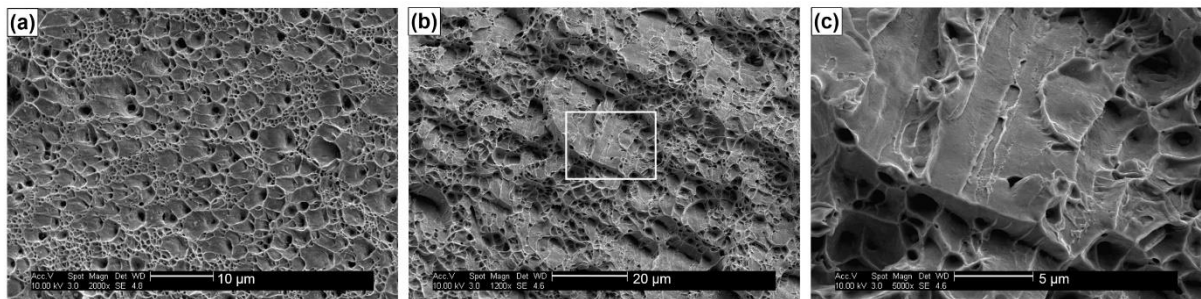


Figure 5-9. SEM images showing the fractographs of tensile fracture surfaces of condition: (a) ST + H900: (b) AD+H900: (c) Magnification of b.

5.4 Discussion.

Alloy 17-4 PH has a Cr_{eq}/Ni_{eq} ratio greater than 1.55, which produces a primary ferritic solidification mode. Under equilibrium cooling, the following phase transformation sequence takes place: $L \rightarrow \delta\text{-ferrite} \rightarrow \gamma\text{-austenite} + \delta\text{-ferrite} \rightarrow \text{martensite} + \delta\text{-ferrite}$ [12]. However, cooling rates inherent to WAAM deposition, limit the amount of $\delta\text{-ferrite}$ that can transform to $\gamma\text{-austenite}$ and it would also vary on the layer number as it will critically dependent on the cooling rate to

promote any solid state diffusion. Hence, some fraction of δ -ferrite will remain at room temperature (**Figure 5-5a**). The same behaviour has been observed before for welding of 17-4 PH [15]. This results in the formation of a dendritic martensite- δ ferrite microstructure for all the AD condition samples analysed in this work. Compositional heterogeneities and microsegregation are expected between dendritic and interdendritic regions, as well as partitioning of solute elements as consequence of solubility differences between phases. After ST, microstructure changes to nearly 100% lath martensite (**Figure 5-5c**). The exposure at temperatures above A_{c3} and the slower cooling rate of the air cooling promote the transformation of most of the δ -ferrite into austenite that can then transforms to martensite. During soaking, sufficient time is given for diffusion to occur and it is expected that dendritic segregation is removed, together with the dissolution of precipitates. Therefore, microstructure under this condition should show more homogenous properties in terms of hardness and tensile strength. However, the solutionised matrix would be softer due to lack of any precipitation hardening as can be seen from the hardness results and tensile test (**Figure 5-7** and **Table 5-3**).

EBSD for phase identification reveals lower percentages of retained austenite for the samples built using SG1 (**Figure 5-6**). A higher heat input and therefore a slower cooling rate is expected when using SG1, due to the presence of He on this gas [24]. Since SG1 provides a higher heat input, it can be suggested that larger grains will grow in this case, in contrast to sample built with SG2. Due to the volume expansion in the austenite to martensite transformation, plastic deformation must occur, therefore the yield stress of the material must be surpassed. Since a decrease in grain size comes together with an increase in yield stress, as established by the well-known Hall-Petch relation, a smaller grain size will lead to a decrease in the martensite transformation start temperature M_s . In other words, smaller grains increase the mechanical barrier to have complete transformation to martensite and gives higher tendency of retaining some austenite [25]. As described in the introductory section of this work, retained austenite can be detrimental for some properties of 17-4 PH. For this reason, SG1 was selected to build the samples for tensile mechanical testing.

It is well known that coherent Cu-rich precipitates are responsible for the increase of hardness in 17-4 PH [15]. Results from **Figure 5-7a** and **b** allow us to establish that an increase of hardness can be obtained by ageing directly on AD condition without any ST. Apart from the fact that the precipitation of hardening coherent Cu-enriched particles in the martensite is promoted during ageing, it has been shown by Yoo et al [26] that δ -ferrite can also experience an increase in hardness as a consequence of the nucleation and growth of precipitates. This could explain why in some cases, hardness values for the AD+H900 samples are higher than the ones obtained for ST+H900.

Comparing both deposition strategies for the AD state (**Figure 5-8a**), it can be seen that there is no consistent trend in the hardness values between deposition paths. In other words, for the same shielding gas, in some cases, the hardness for oscillated pass is higher and in others, parallel path shows higher values. This could be a consequence of the repetitive thermal cycles inherent to the WAAM process. As measured by Xiong et al [27], during WAAM of steel, every time a new layer is deposited, the temperature can increase repetitively to at least 450 °C, even if the heat source is already well away in a subsequent layer. Hence, as different regions of the build will experience different thermal cycles, some of these regions could have a different degree of ageing (underaged, aged or overaged). Therefore, hardness measurements show a fluctuating behaviour depending on the amount and size of Cu-enriched precipitated particles. It was identified that, in all cases, ST samples show lower hardness compared to AD condition. This helps to further support that during WAAM deposition some degree of particles precipitation takes place during the repetitive thermal cycling. Through ST, all the precipitates are expected to dissolve back into solid solution, creating a softer and homogeneous microstructure (error bars become smaller for ST samples as compared to AD).

From **Figure 5-8b**, it is evident how the differences in hardness are negligible after ST is applied, regardless of the deposition strategy or the shielding gas used. This is a consequence of the more homogeneous morphology obtained after solution treatment, as previously explained. Additionally, hardness profiles become almost horizontal lines, meaning that differing degree of ageing that

could exist in different regions of the samples becomes uniform by the ST. Therefore, we propose that the final hardness of WAAM 17-4 PH manufactured components can be carefully adjusted by post-deposition thermal treatment, independent of the deposition path or shielding gas used. Tensile test results helped to further analyse the influence of different phases such as lath martensite and δ -ferrite on mechanical properties.

It was only possible to achieve the required tensile properties by applying solutionizing heat treatment prior to ageing. This condition guarantees a homogenous microstructure of nearly 100% lath martensite where segregated elements and precipitates have dissolved back into solid solution during ST. Additionally, upon ageing, precipitates nucleation and growth will take place evenly, producing the expected tensile behaviour (**Table 5-3**, ST + H900). This is the reason why a ST prior ageing proved to be successful in this work in order to get the required minima for tensile properties. Fracture surface morphologies are consistent with the tensile test results. The sample in ST + H900 condition showed a fracture dominated by a large number of round or equiaxed dimples (**Figure 5-9a**), which corresponds to the ductile behaviour of a 13.8% elongation value. A more detailed analysis of **Fig. 5-9a** shows a network of smaller dimples, this is probably related to the voids initiating in very fine second phase particles generated during the ageing step [28].

The significant drop of nearly 50% in ductility between AD+H900 and ST+H900 condition can be attributed to the highly heterogeneous nature of the microstructure in the AD state. Segregation and solute partitioning will produce phases with different strength and hence, different behaviour to uniaxial tensile load. We can also suggest that a further increase of precipitates in the δ -ferrite phase during ageing might reduce the ductility. Several authors have reported that δ -ferrite embrittlement is possible as consequence of nucleation and growth of precipitates in this phase. The mechanism of δ -ferrite embrittlement has been described only for long exposure ageing at 400 °C [29]; where precipitates can grow and change from rounded shape to rectangular shape which is associated with severe embrittlement. However, the repetitive thermal cycles during WAAM deposition may expose certain regions to higher temperatures that could be

equivalent to prolonged 400 °C ageing. This is not the case after ST, as these particles can dissolve back into solid solution, and they will only grow marginally in the subsequent ageing treatment. Additionally, volume fractions of δ -ferrite tend to reduce by exposition to temperatures above A_{c3} [26]. Hence, after ST, no δ -ferrite phase is available for any subsequent embrittlement. Fracture morphology showed in **Figure 5-9c** serves as evidence of dendritic segregation and possible localized δ -ferrite embrittlement, as some regions exhibit cleavage facets characteristic of brittle behaviour in combination with ductile areas.

Direction-specific results showed some differences in terms of strength and elongation. However, the t-student test only showed a statistical significance difference only for of the UTS value of AD + H900 samples (**Table 5-3**). This anisotropic response is related to the columnar microstructure observed in **Figure 5-5b**. This characteristic has been observed before for WAAM of other materials such as Ti-6Al-4V, where columnar grains have also been identified [30]. For solution treated and aged samples no anisotropy was observed as the columnar macrostructure is eliminated during thermal processing (**Figure 5-5c**).

5.5 Conclusions.

From the different characterisations performed, the following conclusions can be drawn:

- As deposited WAAM 17-4 PH is formed of a dendritic martensite- δ ferrite microstructure, with very small percentages of retained austenite. This dendritic microstructure is expected to have compositional heterogeneities and microsegregation between dendritic and interdendritic regions. After solution treatment, the as-deposited grain structure broke during re-austenisation and on subsequent cooling transforms to nearly 100% lath martensite with minimal segregation.
- Retained austenite formation as a micro-constituent is critically dependant on the cooling rate and therefore on the heat input during deposition.

- Solutionizing and ageing develop the combination of tensile strength and ductility required for 17-4 PH which makes it independent of the processing parameters and the deposition strategy adopted during building.
- Deposition strategy and shielding gas produces various hardness profiles with no consistent trend. However, the properties are effectively homogenised after the suitable heat treatment. No volumetric defects were identified on any of the manufactured samples on this study.
- Direct ageing (no prior solution treatment) on the as-deposited condition resulted in a reduction of ductility by nearly 50%. It is suggested that the δ -ferrite phase embrittlement is contributing to the ductility drop after direct ageing on the as-deposited condition. Localized brittle facets found in the fractographs corresponding to these samples serve as evidence of this mechanism.
- Anisotropy in tensile behaviour was identified only for the ultimate tensile strength of as-deposited samples with only an ageing treatment.

5.6 References.

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6 Microstructural characterisation and mechanical properties of Ti-5Al-5V-5Mo-3Cr built by WAAM and the effect on microstructural evolution of different thermal cycles and post-deposition heat treatment.

This chapter is based on the following publication. However, additional results have been added regarding the effect of different thermal cycles and post-deposition heat treatment on the microstructural evolution and mechanical properties of WAAM Ti-5553.

A. Caballero, A.E. Davis, Kennedy J.R, J. Fellowes, A. Garner A, S. Williams, P. Prangnell. *Microstructural characterisation and mechanical properties of Ti-5Al-5V-5Mo-3Cr built by wire and arc additive manufacture*. Philosophical Magazine. (2022). doi: <https://doi.org/10.1080/14786435.2022.2113470>.

In this chapter another age-hardenable alloy, Ti-5553, was investigated by applying a similar approach to the previous chapter. The characteristics and behaviour of Ti-5553 deposited by WAAM were studied and reported for the first time in the literature. The role and criticality of different thermal cycles were also investigated. In contrast to the findings on 17-4 PH, WAAM deposited Ti-5553 showed a strong dependence between the process thermal cycles and the developed microstructure. The response to post-deposition heat treatment was also investigated and it was concluded that its optimisation is key to obtaining satisfactory mechanical properties.

Abstract: the as-deposited microstructure and mechanical properties of the near- β titanium alloy Ti-5Al-5V-5Mo-3Cr (Ti-5553) produced by wire-arc additive manufacture (WAAM) were investigated, to understand its microstructural evolution under WAAM deposition conditions and to establish correlations between the microstructure features formed and the thermal cycles experienced during deposition. The influence of different thermal cycles on microstructural evolution and the effect of post-deposition heat treatment was also considered. The initial ‘as-deposited’ Ti-5553 WAAM material exhibited higher tensile strengths than other as-deposited additively manufactured Ti-5553 deposits

previously reported in the literature, but had significant anisotropy in elongation, as a consequence of the coarse and columnar β -grain structure that formed on solidification, which exhibited a strong $\{001\}_{\beta} <001>_{\beta}$ cube texture. The multiple reheating cycles, inherent to the WAAM process, were recorded using a novel 'harpoon' thermocouple technique, and the α precipitation evolution was related to the thermal history. Electron probe microanalysis chemical maps revealed significant solute microsegregation during solidification, which influenced the subsequent precipitation due to its effect on the local β -phase stability. As each layer experienced more reheating cycles, the microstructure evolution could be 'time resolved' and the α -laths were found to precipitate in a specific sequence of nucleation sites, starting at the β -grain boundaries and then inter-dendritically, where there was lower matrix β stability. However, after the reheating peak temperature was insufficiently high to have any further effect, the microstructure consisted of a relatively uniform distribution of α laths. In an effort to minimise the anisotropy for the elongation before the heat treatment was applied, the coarse and columnar β grain structure was refined by increasing the wire feed speed during WAAM deposition. Nevertheless, refining the grains proved to generate additional limitations through the formation of brittle GB α /precipitation free zones that caused the nucleation and coalescence of microcracks that led to an intergranular/transgranular brittle fracture mode. This highlighted that tailored heat treatments need to be developed to optimise the microstructure and mechanical performance of WAAM-deposited Ti-5553.

Keywords: additive manufacture, titanium, phase transformation, texture.

6.1 Introduction

The alloy Ti-5Al-5Mo-5V-3Cr-0.5Fe (Ti-5553, wt.%) is a modification of the Russian-developed near- β titanium alloy VT-22 and can offer strengths as high as 1300 MPa in thick section aerospace components [1], [2]. The use of this alloy has grown substantially during the last 15 to 20 years, thanks to its outstanding deep-hardenability and its retention of useful levels of ductility and toughness after heat treatment [1], [3]. In addition, although significantly more expensive, β -stabilized titanium alloys like Ti-5553 offer other advantages over the more

commonly used α - β titanium alloys like Ti-6Al-4V (Ti-64), such as increased high-cycle fatigue properties [1]–[3]. Ti-5553 is therefore an attractive alloy to investigate for near-net-shape additive manufacturing (AM) applications.

The greater strength of alloys like Ti-5553 arises from the controlled decomposition of the metastable β phase, which in conventional products occurs through solution and ageing heat treatments that produce a uniform distribution of fine α -phase lath-morphology precipitates. Due to the greater concentration of β -stabilising elements (V, Mo, Cr), the lower β -transus temperature, and presence of slow diffusing elements like Mo, diffusional phase transformation kinetics in Ti-5553 are slower than in Ti-64, allowing the metastable- β phase to be retained at room temperature with relatively slow cooling rates [1], [3]–[5]. In addition, the metastable- β solid solution can decompose by multiple transformation pathways that are highly dependent on the thermal conditions, including heating rate, cooling rate, and time at temperature [1], [3]–[7]. In AM, in the as-deposited state, a greater level of microsegregation is also expected within the parent β grains in Ti-5553 than in Ti-64, due to the greater deviation of the partition coefficients of the main alloying elements Mo and Cr from unity [8]–[12]. As a result, the AM microstructures of as-deposited Ti-5553 differ greatly to those of Ti-64 and are highly dependent on the cyclic thermal conditions experienced during a specific AM process, which will have a varied effect on the final microstructure and mechanical properties of the as-deposited material [12]–[18].

To date, studies of the microstructure of Ti-5553 produced by AM have only focused on higher-energy-density laser and powder-based processes (e.g. [12], [14]). Some of this work has focused on the processability of Ti-5553, to obtain high density parts, while other studies have focused on metallurgical aspects of the microstructure development under different AM conditions [12]–[17], [19], [20]. The as-deposited solidification microstructure is typically reported to develop with coarse, columnar β -phase grains elongated in the average solidification direction [12], [16], [18]. Due to the rapid thermal cycles in AM processes, the presence of the α phase, which precipitates below the β transus after

solidification, has only been found during certain build conditions. In the powder bed and laser directed energy deposition (DED) processes studied to date, α precipitation has only been seen when higher heat inputs are used, or where a higher build temperature is maintained by heating the base plate [12], [14], [16]. Thus, it is evident that the heat input, energy density, and thermal cycles experienced during AM play an important role in controlling the as-deposited transformation microstructure of Ti-5553, which strongly influences its mechanical properties.

High-deposition-rate, wire-fed, plasma-arc-based AM has significant advantages for producing larger scale titanium components; however, no studies have been previously published on Ti-5553 (to the authors' knowledge). We have recently reported on the microstructure transition seen between Ti-5553 and Ti-64 in alloy-alloy composite WAAM deposits [18], but the effect on the evolution of the transformation microstructure in a near- β alloy has not yet been fully characterized. It is therefore important to explore the phase transformation behaviour in this alloy during an additive process that involves a more diffuse heat source, relatively larger melt pool and significantly lower cooling rates (<100 °C/s) [12], [14], [17], [21]–[27]. In addition, there is currently only very limited information available in the literature on the interaction between Ti-5553 and arc heat sources in the context of arc welding [28].

The present study, therefore, seeks to improve understanding of the as-deposited microstructural evolution of Ti-5553 during the complex, but slower, cyclic heating and cooling rate thermal history of a typical high-deposition-rate AM process, capable of building large aerospace components. In this paper, in-depth multiscale microstructure characterisation has been performed, using a range of techniques, including optical microscopy, electron backscatter diffraction (EBSD), transmission Kikuchi diffraction (TKD) and electron probe microanalysis (EPMA), to fully understand both the effects of the solidification microstructure and subsequent thermal cycling on the α precipitation behaviour in a wire and plasma arc AM process. The full temperature cycle during deposition was recorded, using a novel 'harpoon' technique, so that correlations could be established between

the microstructure development and thermal history. In addition, the influence of different thermal cycles on microstructural evolution and the effect of post-deposition heat treatment on the final mechanical properties were also investigated.

6.2 Materials and Methods.

Several samples were manufactured to investigate various aspects of the behaviour of Ti-5553 during WAAM deposition. Firstly, a single pass sample was built to perform an initial detailed microstructural characterisation and correlate it with the tensile behaviour. Secondly, two more single pass samples were manufactured using different thermal cycles in order to assess the sensitivity to the developed “as-deposited” microstructure to different thermal histories. Finally, four more samples were manufactured to investigate the role of post-deposition heat treatments as a way to optimise the microstructure and mechanical properties. A solution and ageing treatment were applied to the samples, followed by tensile mechanical testing. These last four samples were manufactured using a higher wire feed speed in order to obtain a more refined β -grain structure.

6.2.1 Manufacture of single pass sample for detailed microstructural characterisation and mechanical testing.

A single pass wall was deposited using a PTA welding power source attached to a 6-axis industrial robot. In order to provide an inert atmosphere to minimise oxygen pick up, deposition was performed inside a flexible shielding tent filled with argon. An oxygen concentration level of approximately 800 ppm was maintained during deposition and monitored by an oxygen analyser. The sample was built using an average current of 160 amps, travel speed of 5 mm/sec, and wire feed speed of 1.8 m/min. The torch stand-off distance was 8 mm, with an argon plasma gas flow rate equal to 0.8 l/min, and a shielding gas flow rate of 15 l/min. The composition (wt.%) of the Ti-5553 1.2 mm diameter wire used was Al 5.0%, V 4.92%, Mo 4.86%, Cr 2.89% Fe 0.43%, O 0.129%, C 0.007% and N 0.002% with a balance of Ti. The manufactured wall had final dimensions of approximately 9 x 130 x 310 mm and was deposited on an 11 mm-thick Ti-64 substrate. During deposition, the heat source travel direction was alternated

(backwards and forwards) in every layer. A schematic diagram of the deposition process and an image of the built wall are presented in **Figure 6-1**.

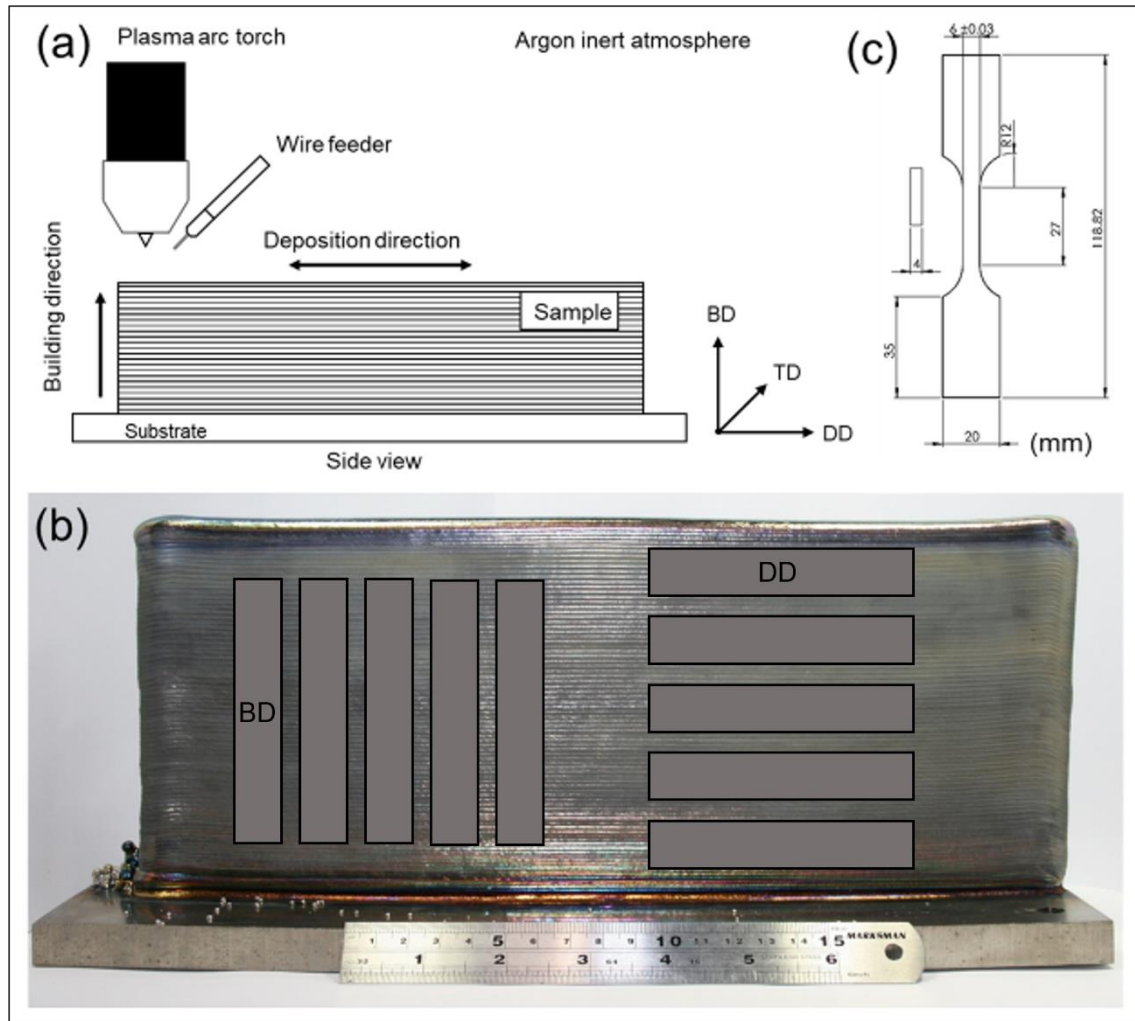


Figure 6-1. (a) Schematic representation of the experimental setup (the reference system is defined as: building direction (BD), transverse direction (TD), and deposition direction (DD)); (b) the manufactured sample and schematic of coupon layout on the wall, and (c) geometry and dimensions of the uniaxial tensile specimen used.

6.2.2 Manufacture of samples with different thermal cycles.

The two single pass samples manufactured to study the variation of microstructure with different thermal cycles were built using the same parameter described in the previous section. However, these samples were 150 mm long and were formed by a total of 20 layers. To induce distinctive thermal cycles,

different interlayer temperatures were used. One of the samples was built with a constant interlayer temperature of 50 °C, while the other one was built using an interlayer temperature of 200 °C. The thermal histories were measured using the method described in section 6.2.4 and the thermocouples were inserted in layer number 6 and the thermal data was recorded from layer 7 onwards.

6.2.3 Manufacture of samples for post-deposition heat treatment investigation.

Four samples were manufactured to study the effect of post-deposition heat treatment on microstructure and mechanical properties. Two samples were manufactured using a single pass deposition strategy and two more using an oscillated pass deposition strategy (see **Figure 5-1** for reference). The oscillated pass samples were built to reproduce more accurately the manufacturing conditions of components requiring wider wall thickness than the single pass approach can provide. It has been reported that increasing the wire feed speed during WAAM deposition can be used as a method to refine the β grain structure [48]. Hence, this approach was implemented as an attempt to refine the β grain structure. To achieve higher wire feeding rates a dual wire feeding system was used to manufacture these samples. The samples were built using an average current of 140 amps, travel speed of 5 mm/sec, and wire feed speed of 4.2 m/min. For the oscillated samples, an oscillation width of 19 mm and a step advancement of 4.3 mm were used. The rest of the parameters were the same described in the previous section.

The heat treatment applied was selected based on the information available in the literature. The target was to achieve a high strength condition, around 1300MPa for the UTS, with an Elongation between 4-6%, which is normally the requirement for Ti-5553 landing gear components. Solution treatment was performed at 1000°C for 15 minutes followed by ageing at 600 °C for 8 hours. The cooling rate applied after solution treatment was air cooling. This was selected with the aim of simulating the cooling rates that components with a considerable thickness would experience at the core of the material. The whole of the heat treatment was conducted in air, but the tensile coupons were later extracted from

the blanks in order to minimise the potential embrittle experienced due to oxygen pick up. The oxygen content of the final sample after heat treatment was of 0.17 wt.% (which still under the maximum oxygen concentration allowed for titanium alloy of 0.2wt%). The recorded thermal data for the solution heat treatment and subsequent ageing is presented in **Figure 6-2**. The cooling rate after solution treatment was recorded and was calculated to be $\sim 0.15^{\circ}\text{C}/\text{sec}$. The heating rate to achieve the target ageing temperature was $0.1^{\circ}\text{C}/\text{sec}$. The small discontinuity on the heating ramp for the solution heat treatment shown in the graph was caused by some noise in the data acquisition and does not represent an interruption of the actual heat treatment. The data was recorded by attaching a k-type thermocouple to the centre of a dummy Ti-5553 wall of the same thickness as the oscillated pass samples manufactured. Mechanical tensile testing was performed in the as-deposited condition, and after the heat treatment was applied. The conditions for the mechanical testing are detailed in section 6.2.5.

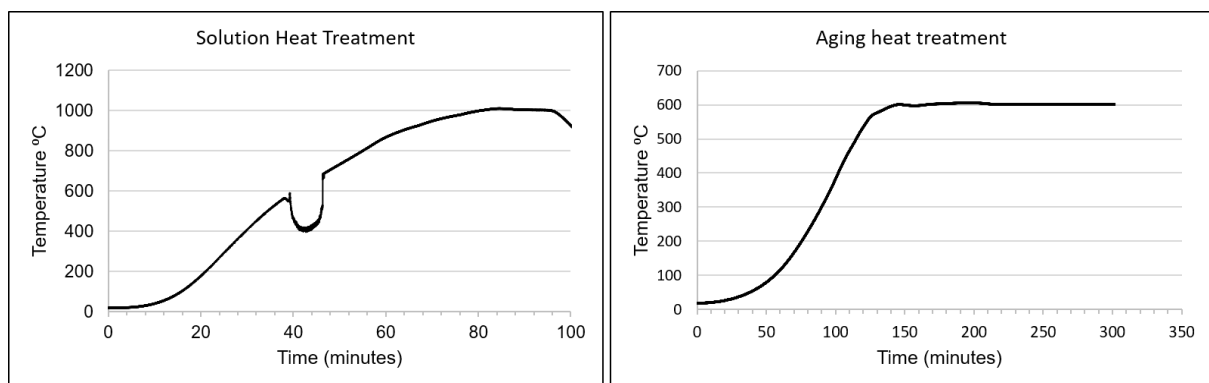


Figure 6-2. Recorded thermal data of the applied heat treatment.

6.2.4 Thermal cycle measurement.

The thermal history of the deposits was measured, in order to correlate it with the microstructural evolution during deposition, using a novel in-house developed thermocouple 'harpooning device'. This device enabled a type-R thermocouple to be automatically plunged into the centre of the melt pool with precise positioning during deposition. To the authors' knowledge, this is the first time this type of device and experimental approach have been used to acquire thermal data during the WAAM processing of a titanium alloy. A schematic of the device used, and a still image of the inserted thermocouple can be seen in **Figure 6-3**.

The harpooning action of inserting the thermocouple into the melt pool was achieved by using a linear pneumatic actuator attached to a set of high precision linear stages that allowed accurate adjustments of the thermocouple position. At the same time, a solenoid type valve was interfaced with the robot motion system, which allowed the insertion of the thermocouple in the exact desired location. After insertion at the central line of a melt track, the thermocouple solidified in place. This enabled accurate measurement of the thermal cycles experienced at the selected location during the deposition of subsequent layers. The data was recorded using LabVIEW with a data acquisition rate of 10 Hz.

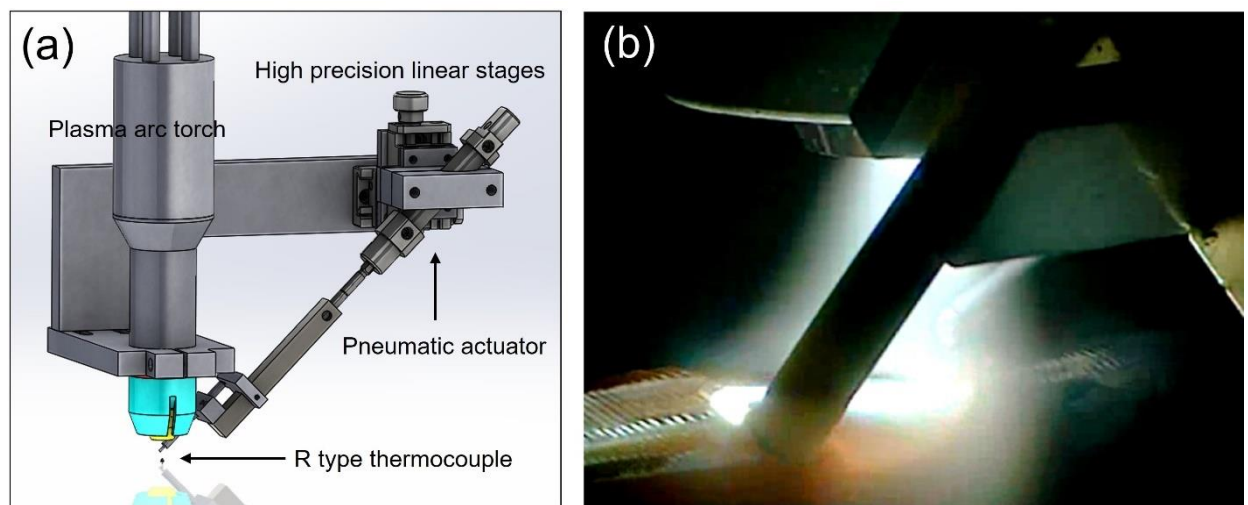


Figure 6-3. (a) Schematic of the harpooning device used in this work. (b) Still image showing R-type thermocouple inserted into the melt pool using the harpooning device.

6.2.5 Mechanical Testing.

Tensile tests were performed under the guidelines of the BS EN 2002-1:2005 standard [29] using an Instron 5500R electromechanical test frame, equipped with a load cell of 100 kN and an extension rate of 0.2 mm/min. Tensile coupons were machined out of the WAAM manufactured samples with the test direction both in the vertical build direction (BD) and horizontally, parallel to the wall (DD). The coupons layout on the wall can be seen in **Figure 6-1b**. Five samples from each orientation were tested and the proof stress, ultimate tensile strength, and

elongation to failure were averaged, with errors given as one standard deviation. The geometry of the tensile coupon used is indicated in **Figure 6-1c**.

Vickers hardness maps were acquired automatically across the centre of the BD-TD plane with a Struers Durascan 80 hardness tester, using an array of indents with a 0.4 mm pitch, with an applied load of 0.1 kg and a 10 s dwell time. The hardness vs build height profile was produced from the array data by averaging the points in the sample transverse direction (TD) and given 95% confidence intervals.

6.2.6 Microstructural characterisation.

A transverse direction (TD) section of the top 24 mm of the first built wall was extracted for microstructural characterisation, representing the last ~20 layers deposited. Metallographic preparation of the sample was carried out using the procedure outlined by Voort [30] and etched with Kroll's reagent. Optical microscopy was performed using a Zeiss Axio Imager 2, with automated stage scanning to produce a large-scale, high-resolution, stitched macrograph.

Scanning electron microscopy (SEM) imaging and electron backscatter diffraction (EBSD) orientation maps were obtained on unetched, polished samples using a TESCAN Mira3 FEG-SEM, equipped with an Oxford Instruments' Symmetry EBSD detector and AZtec acquisition software, with an accelerating voltage and beam current of 20 kV and 48 nA, respectively. EBSD data was processed using Oxford Instruments' AZtec Crystal software and maps are displayed throughout with inverse pole figure (IPF) colouring (reference direction BD), with low ($>5^\circ$) and high grain boundaries ($>15^\circ$) highlighted in white and black, respectively. Contoured pole figures were also produced and scaled in multiples of random density (MRD).

For the higher resolution TKD analysis, a 3 mm diameter sample was punched from a ~110 μm foil and electropolished at a voltage of 17 V in a 5 % perchloric acid and methanol electrolyte at -40°C . TKD was carried out on a FEI Magellan 400L FEG-SEM, using an accelerating voltage of 30 kV, with the sample tilted to a 20° angle away from the EBSD camera at a working distance of 2 mm.

EPMA was performed with a JEOL JXA-8530F FEG-EPMA, equipped with 4 wave dispersive spectrometers (WDS), and was used to map the chemical segregation throughout the WAAM build. Large-area qualitative (count rate) and quantified smaller maps were obtained using an accelerating voltage of 15 kV, a current of 100 nA, and a 1 and 5 μm step size was used for the small and large-area maps, respectively. The aluminium ($K_{\alpha 1}$) signal was collected on a TAP diffraction crystal, Mo ($L_{\alpha 1}$) on a PET, and Fe ($K_{\alpha 1}$), Cr ($K_{\alpha 1}$), and V ($K_{\beta 1}$) on a LiFL crystal.

6.3 Results.

6.3.1 Overview.

Representative tensile test results from the Ti-5553 WAAM samples, machined from the steady-state region of the deposit, are shown in **Figure 6-4**. Average values for the coupons tested in each orientation (BD and WD) are also summarised in **Table 6-1**, along with other results reported in the literature for AM processes and a baseline comparison to conventional wrought products. The as-built proof stresses of the test samples were in the range of 1040 – 1070 MPa, which is comparable to the lower end of that reported for fully heat treated wrought Ti-5553 materials when in a standard solution-treated and aged condition [2]. However, the as-deposited proof stresses of the WAAM samples surpassed those reported for Ti-5553 AM builds produced by laser-based processes by ~30 %, whilst still maintaining comparable elongation to failure (see **Table 6-1**). At 21 %, the average elongation to failure in the build direction of the Ti-5553 WAAM samples was also high for this strength level, but it was 2.5 times lower in DD (~8 %). In addition, in BD, the stress-strain curves showed limited strain hardening and the elongation mainly occurred in a diffuse neck; whereas in DD, strain hardening was evident, but the samples failed abruptly without significant necking.

Table 6-1. Summary of the tensile test results for coupons extracted parallel to the build (BD) and deposition direction (DD). PS: 0.2 % proof strength; and UTS: ultimate tensile strength. Tensile properties of various Ti-5553 AM deposits (both powder bed and DED) and wrought forged components are included for comparison.

WAAM	PS (MPa)	UTS (MPa)	Elongation (%)	Reference
Build direction (BD)	1048.1±11.4	1064.9±10.4	21.0±1.4	This work
Deposition direction (DD)	1036.4±13.7	1094±1.0	8.3±3.2	This work
Published Laser-PBF AM processes				
As deposited	755-800	769-800	9-18	[15], [17]
Aged 600°C	925-1375	1112-1375	2-14	[4], [15], [27], [31]
Aged 700-750°C	1050	1050-1075	9-19	[15], [28]
Aged 800-850°C	900-975	900-975	16-20	[27], [31]
Wrought (inc. ST & aged)	1090-1300	1145-1386	5-16	[2], [3]

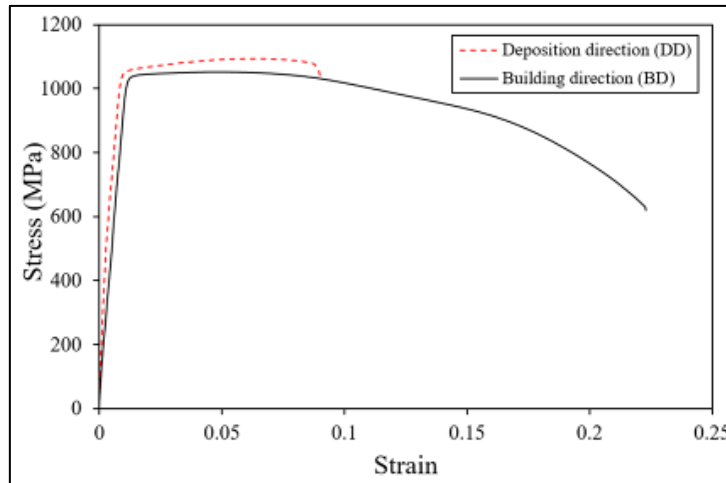


Figure 6-4. Typical strain-stress curves measured in the deposition (DD) and building direction (BD) orientations.

Given that Ti-5553 is conventionally solution heat-treated and aged to obtain its optimum mechanical properties, the thermal history of the Ti-5553 WAAM test builds were recorded to better understand the conditions that gave rise to α precipitation during deposition. The thermal history recorded during deposition, measured by the harpoon method, is presented in **Figure 6-5**. This starts from the point where the type R thermocouple was inserted into the melt pool and shows the thermal cycles caused by subsequent deposition of 15 added layers. It can be seen that the peak temperature recorded of $\sim 1450^\circ\text{C}$, when the thermocouple was first inserted, is near the maximum detectable temperature of a type R thermocouple, so the first temperature peak in the melt pool was not correctly recorded. During the subsequent heating cycles, where the thermocouple was embedded in the solid material, the peak temperature decreased in each cycle, passed through the β transus after 9 layers ($\sim 850^\circ\text{C}$ [32], [33]), then fell to $\sim 650^\circ\text{C}$ by the addition of layer 15. The build-up in the minimum temperature can also be noted in **Figure 6-5** as more layers were added.

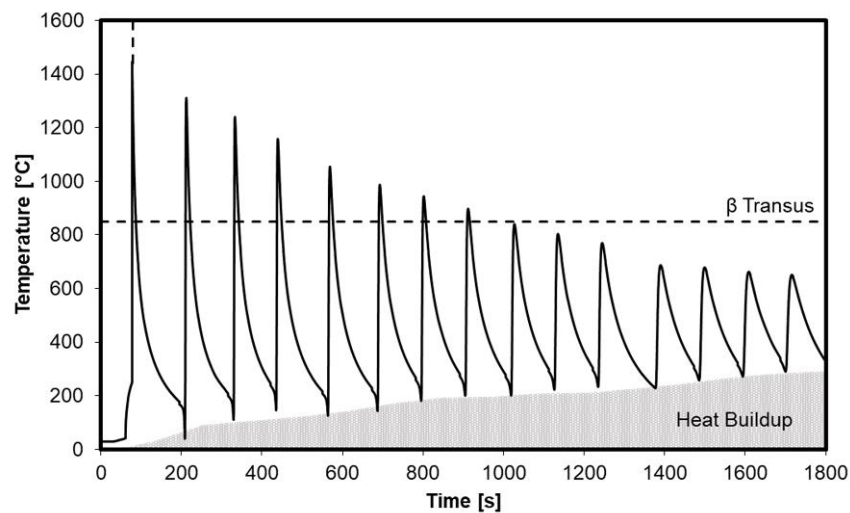


Figure 6-5. Measured thermal history during WAAM deposition of the sample for microstructural characterisation.

An overview optical macrograph of the Ti-5553 WAAM build, cross sectioned in the BD-TD plane, is shown in **Figure 6-6** to demonstrate the impact of this cyclic thermal history on the microstructure. This figure shows the upper 24 layers deposited in the sample and the microstructure evolution throughout, from solidification of the last (top) layer through the subsequent thermal cycles experienced by previously deposited layers as new layers were added, until the temperature fell sufficiently such that no further changes occurred. The dark curved lines labelled in the lighter etched top section are caused by a thin fusion boundary segregation band [22] and can be used to identify each individual layer. Interdendritic microsegregation and the coarse, columnar β grains are also more apparent in the top, lighter etched, part of the sample, with the microsegregation most apparent near the top surface. The analysis presented hereafter focuses on this top region of the as-built sample where the final microstructure evolves and the regions relating to the higher resolution figures shown below are indicated in **Figure 6-6**. **Figure 6-6** also shows a strong etching contrast change between the top and bottom regions of the build, separated by a heterogeneous transition region, which occurred due to precipitation of the α phase. By correlation between the thermal history and the optical image layers, it can be seen that the α phase only starts to precipitate in cycle 12 when the peak temperature at the thermocouple position was <700 °C, but it should be noted that the peak

temperature gradient within a single deposited layer during reheating is significant. This confirms that the α phase precipitates predominantly during subsequent reheating high in the sub-transus region, rather than during cooling in the last cycle from above the β transus (layer 9); i.e. because the β phase is more stable than in alloys like Ti64, and Ti5553 is not particularly quench sensitive, it does not transform on cooling through the β transus.

Higher magnification optical micrographs of the β -annealed top layers, the transition region where the α begins to nucleate, and the microstructure in the bottom steady-state section are presented in **Figure 6-7**, to show the different regions of α precipitation in more detail. In the dark etched region at the bottom of the sample (**Figure 6-7f**), although the α precipitates are too fine to be resolved by optical microscopy, the micrograph appears homogeneous. In contrast, α , as evidenced by regions of darker contrast, is seen to first develop heterogeneously within the transition region, with the images suggesting a preference for earlier α precipitation at the β -grain boundaries (**Figure 6-7b-c**) as well as within the interdendritic regions (**Figure 6-7d**).

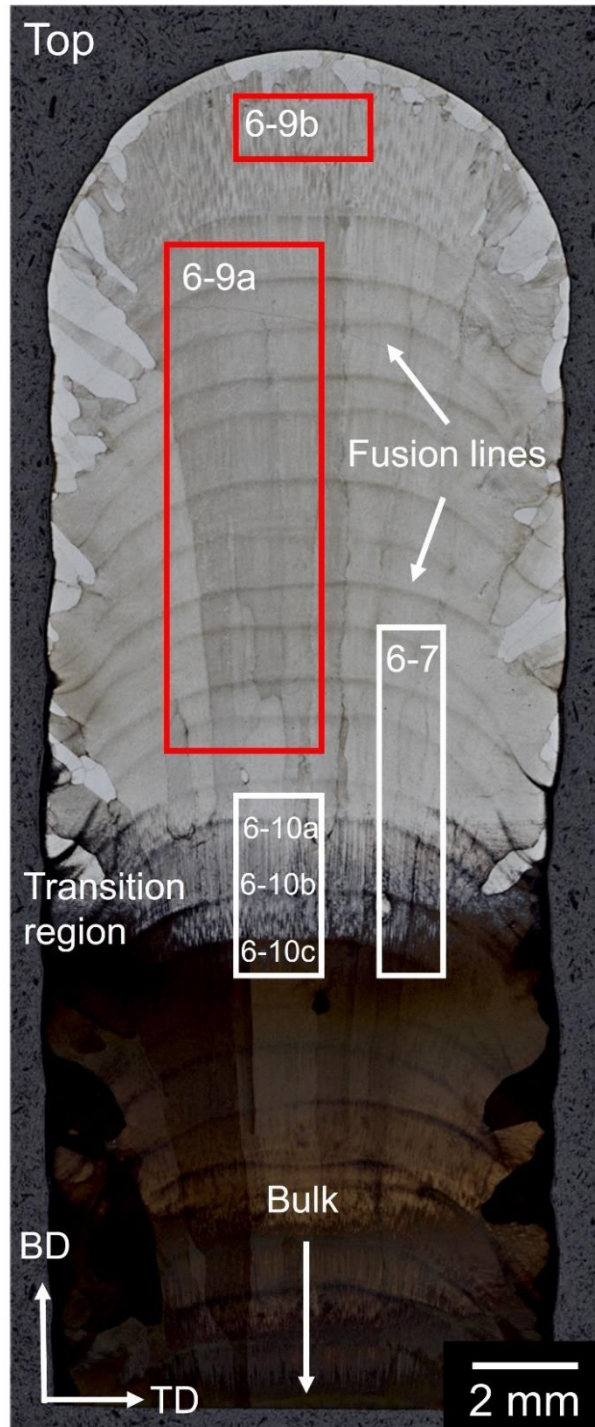


Figure 6-6. Overview optical macrograph of the etched Ti-5553 sample in a transverse (BD-TD) cross section, showing the areas examined in Figures. 6-7, 6-9, and 6-10.

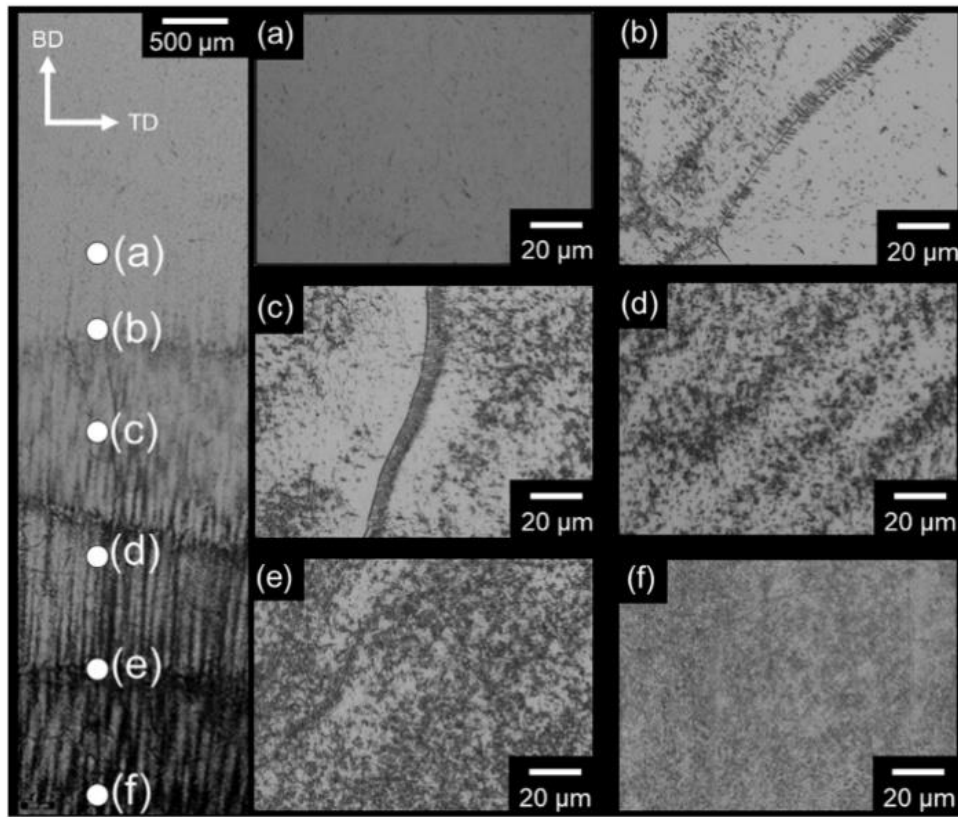


Figure 6-7. Higher magnification optical images showing the evolution of the microstructure across the transition zone between the top metastable- β region and dark etched bottom section with α precipitation seen in Fig. 6-5. The left micrograph indicates the image locations (area indicated in Fig. 6-6) shown in (a) – (f).

6.3.2 Solidification Microstructure.

EBSD and EPMA maps were used to reveal the nature of the primary β -grain structure and the extent of microsegregation that developed during solidification. A β -phase EBSD orientation map of the upper section of the sample is shown in **Figure 6-8a** where it is evident that the core of the deposited wall contained coarse, columnar β grains that are strongly textured. The grains have strong alignment (34 MRD) of their $\langle 001 \rangle_{\beta}$ directions nearly parallel to BD and TD; such that they exhibit an intense $\{001\}_{\beta} \langle 001 \rangle_{\beta}$ cube texture (**Figure 6-8b**). The grains that do exist within the sample interior are also mainly separated by low angle grain boundaries (white lines) of misorientations $< 15^{\circ}$ – i.e. the core of the deposit can be thought of as being close to a $\{001\}_{\beta} \langle 001 \rangle_{\beta}$ cube orientated single β -Ti

crystal, containing subgrains with a small spread of orientations around BD. However, the wall's outer surface layer exhibited a skin of differently orientated smaller columnar grains [18], and their microtexture can be seen in **Figure 6-8d**. These grains appear to have reorientated to grow closer to normal to the solidification front where they experience a severe curvature towards the build edges, which can be seen from the profile of the fusion boundary segregation bands in **Figure 6-6**. These smaller surface grains are also elongated and tend to have their $\langle 001 \rangle_\beta$ directions aligned closer to $\sim 45^\circ$ to BD. A few small, equiaxed grains with non- $\{001\}_\beta \langle 001 \rangle_\beta$ orientations can further be seen within the wall's coarse and columnar core grain structure. These grains did not grow greatly after formation and were engulfed by the dominant $\{001\}_\beta \langle 001 \rangle_\beta$ orientated columnar β grains during solidification. An example of one of these grain's associated orientations can be found in **Figure 6-8c**. The sample number of grains for the pole figures was limited to 8 grains.

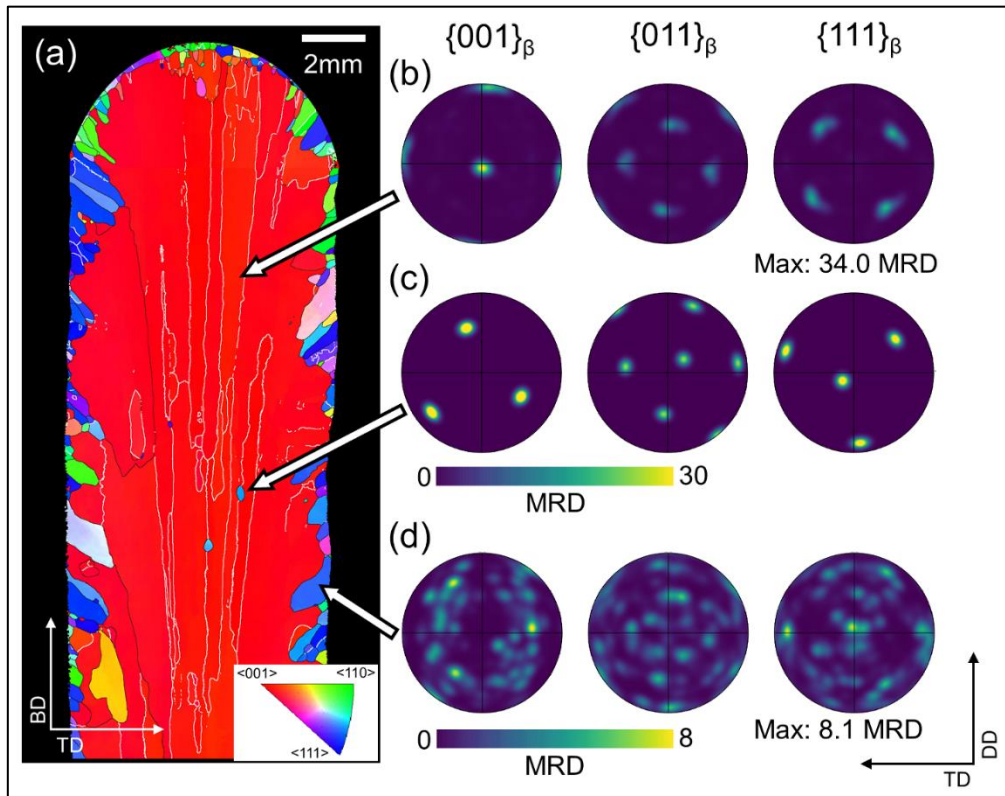


Figure 6-8. The β -grain structure and texture formed on solidification: (a) EBSD inverse pole figure orientation map; and pole figures show (b) the columnar grain

cube texture in the core, (c) an isolated non-cube grain orientation in the core of the deposit, and (d) the microtexture of the surface skin layer of smaller grains.

The extent of solute segregation during solidification can be seen in the EPMA composition map obtained from the upper-sample section in **Figure 6-9**. A 5 μm step size was used in the overview map in **Figure 6-9a**, and a higher resolution 1 μm step size map (**Figure 6-9b**) was acquired from the last layer deposited to better resolve the interdendritic segregation. The strongest interdendritic microsegregation evident in **Figure 6-9a-b** is for Cr and Fe, which have partition coefficients of $k = 0.81$ and 0.79 , respectively [10], [11]. Strong inverse segregation to the dendrite cores is also noted for Mo ($k = 2.0$) [9], [34]. In comparison, Al and V have partition coefficients close to unity [10], [11], [35] and are relatively neutral in terms of their microsegregation; although there is evidence of slight inverse segregation of Al. In **Figure 6-9a**, Cr and Fe can also be seen to have segregated away from the thin horizontal fusion boundary lines that are observed in the etched optical macrograph in **Figure 6-6** and are enriched in Mo.

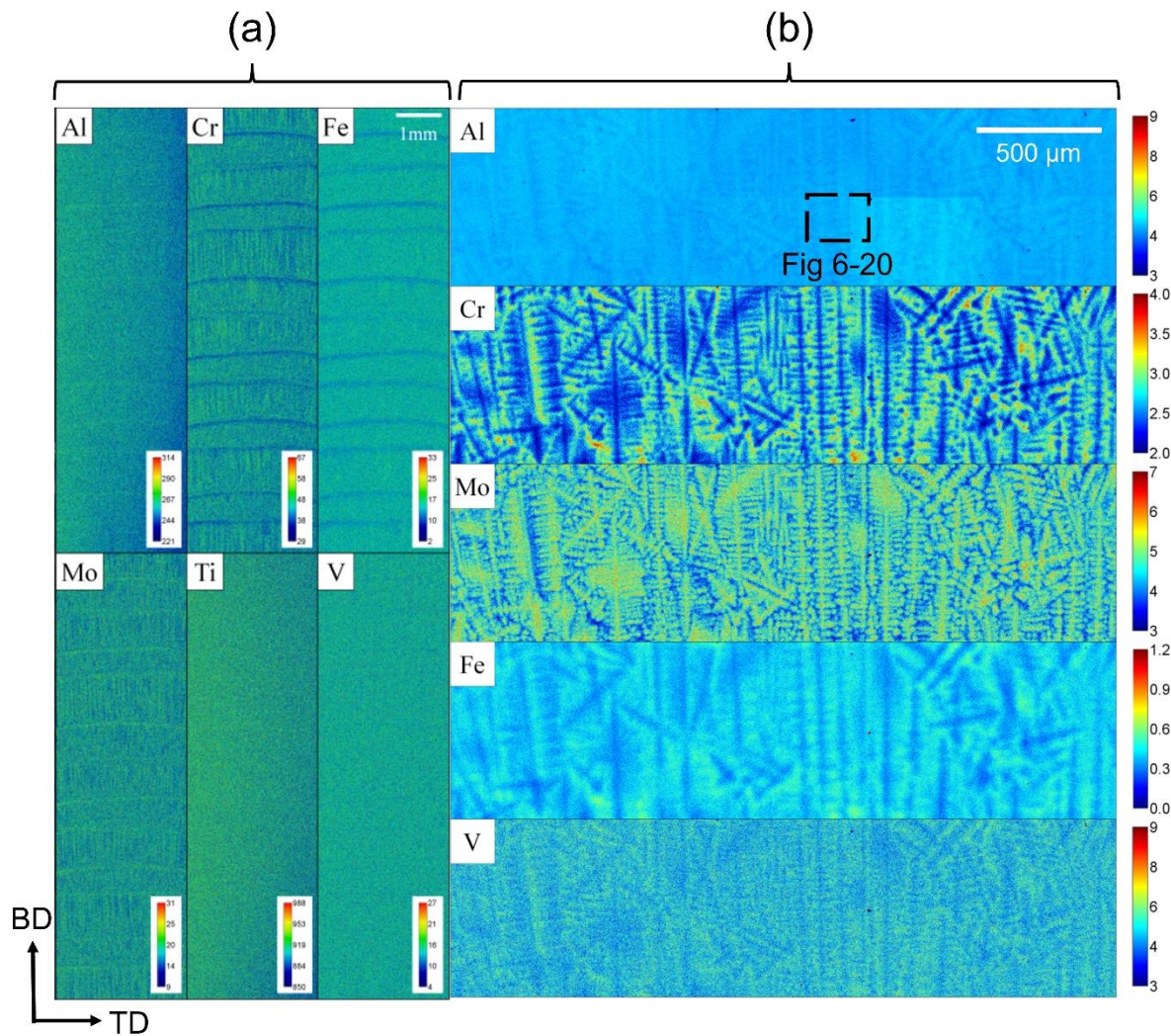


Figure 6-9. Microsegregation in the Ti-5553 deposit revealed by EPMA compositional maps: (a) large step size overviews; (b) higher magnification of the last deposited layer. Note: (a) shows photon count maps where (b) shows quantified elements in wt.%.

6.3.3 Transformation Microstructure.

Higher magnification SEM images of the transition region, and the fully developed transformation microstructure found below layer 15, are shown in **Figure 6-10**. At this magnification, the coarser α -phase precipitation can be resolved and there is a gradual increase in the volume fraction of α laths down the wall through the transition region (**Figure 6-10a-b**), until precipitation stagnates and the microstructure stabilizes as the temperature and supersaturation falls with depth.

It can be seen that the stable bulk ‘as-deposited’ microstructure contains a high volume fraction of ~50 – 150 nm-thick α laths that are relatively homogeneously distributed in the β -phase matrix (**Figure 6-10c**). However, when α first precipitates, it is heterogeneously distributed in clusters with finer laths than those developing in the matrix as the material experiences further lower peak temperature heating cycles.

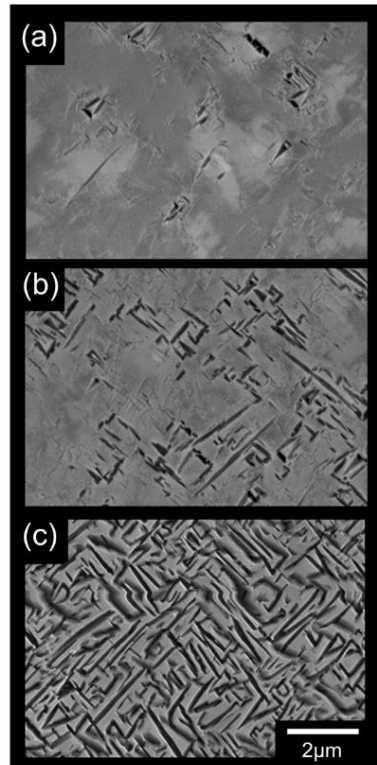


Figure 6-10. Backscatter electron SEM micrographs moving down through the transition region as the α volume fraction increases: (a) (b) (c) taken at the marked locations in Fig. 6-6.

TKD using an electron transparent foil was employed to index the α precipitates, which were too small to be characterized by conventional EBSD. The TKD orientation map acquired for the fully transformed ‘as-deposited’ microstructure region is shown in **Figure 6-11**, along with the α and β -phase map and the phase pole figures. In this map area the β -phase matrix consisted of a single $\langle 001 \rangle_{\beta}$ // BD orientation grain. The α laths did not index well in some areas (coloured black), which is partly a consequence of lattice distortion in the foil caused by relief of the stress induced by the $\beta \rightarrow \alpha$ phase transformation. If these unindexed

points are assumed to also represent the α phase (which is likely given the location and morphology of the unindexed areas), its area fraction was determined to be $\sim 44\%$. In the accompanying pole figures, the α laths can be observed to have adopted all 12 orientations possible via the BOR, which causes a significant dilution of the α texture relative to that of the β phase, and is approximately representative of the near single- β Ti crystal bulk. However, in **Figure 6-11b**, in the $(0001)_\alpha$ pole figure in particular, some variant selection can also be inferred from the observation that some $[0001]_\alpha$ poles having stronger intensities than others. However, without sampling multiple β grains, the effect this has on the overall bulk α texture cannot be commented upon.

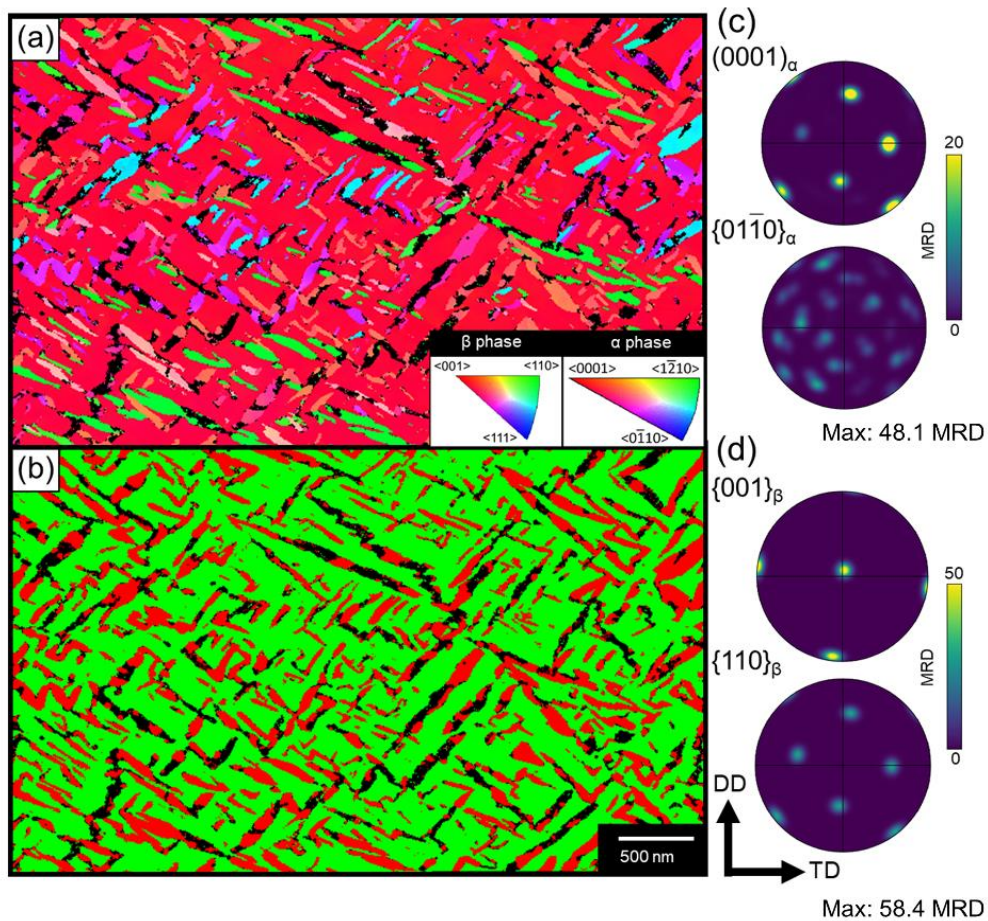


Figure 6-11. TKD maps of the fully developed ‘as-deposited’ α precipitate microstructure: (a) inverse pole figure crystal orientations, (b) phase distributions (red = α phase and green = β phase), and (c) and (d) pole figures for the α and β phase. Black pixels are unindexed points.

6.3.4 Microstructure after different thermal cycles.

The low magnification cross sections on the TD of the samples built with different thermal cycles are presented in **Figure 6-12**. The red dot on each macrograph indicates the location where the thermocouple was inserted. At this magnification, it is possible to identify that there is a change in the α phase precipitation behaviour. As previously described, the dark contrast generated by the etching shows the region where the α phase has precipitated within the β phase matrix. In this case, it can be seen how the sample built with an interpass temperature of 50°C has a more continuous dark region of precipitated α phase, while the sample built a 200°C shows some interruption of the α precipitation pattern (indicated in the figure by a red arrow).

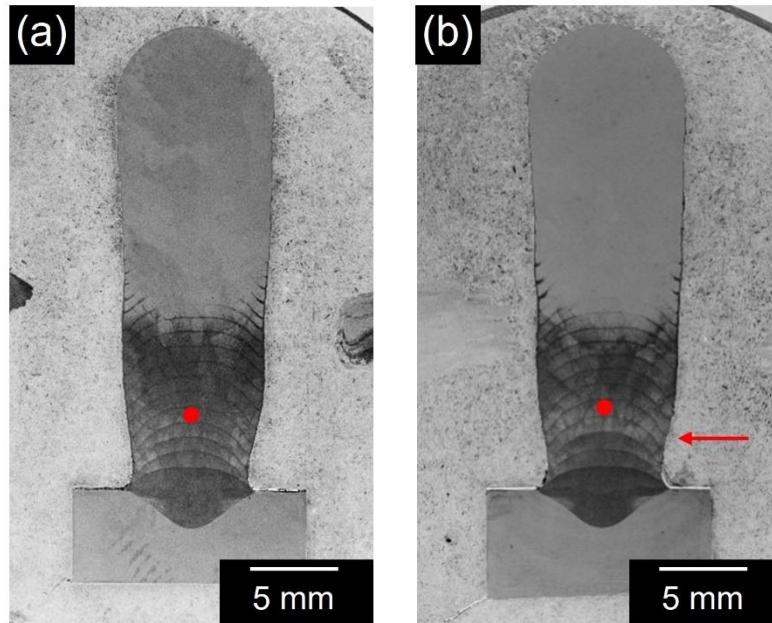


Figure 6-12. Macrographs of samples built with different interpass temperatures: (a) Interpass temperature of 50°C, (b) Interpass temperature of 200°C.

Figure 6-13 shows the high magnification SEM images of the microstructural features at the location of the thermocouple insertion (red dot on **Figure 6-12**). The sample built at 50°C is characterised by finer and higher volume fraction of α phase while the 200°C shows a decreased volume fraction of α with coarser α laths.

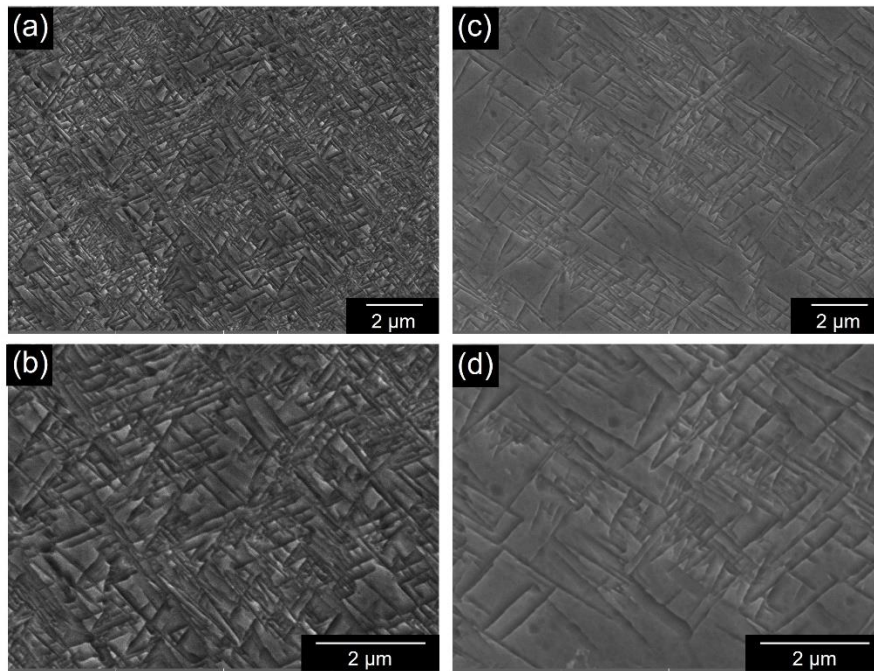


Figure 6-13. SEM micrographs of samples built with different interpass temperature: (a) Interpass temperature of 50°C, (b) Higher magnification of a, (c) Interpass temperature of 100°C, (d) Higher magnification of c.

The thermal histories recorded during deposition, measured by the harpoon method, are presented in **Figure 6-14**. For the interpass temperature of 50°C, the temperature dropped below the β transus after the 9th layer, while it was only until the layer 15th was deposited that the temperature dropped below this point when an interpass temperature of 200°C was used. Meaning that the sample manufactured at lower interpass temperature dwelled for a longer time in the α phase stability region as compared to the other sample. It can also be seen that the peak temperature reached for each cycle for the 200°C sample was higher as compared to the same layer for 50°C. For example, when using an interpass temperature of 200°C the peak temperature for layers 7 and 20 were 1528°C and 555°C, respectively. On the other hand, for the interpass temperature of 50°C, the peak temperature was 1101°C for layer 7 and 410°C for layer 20.

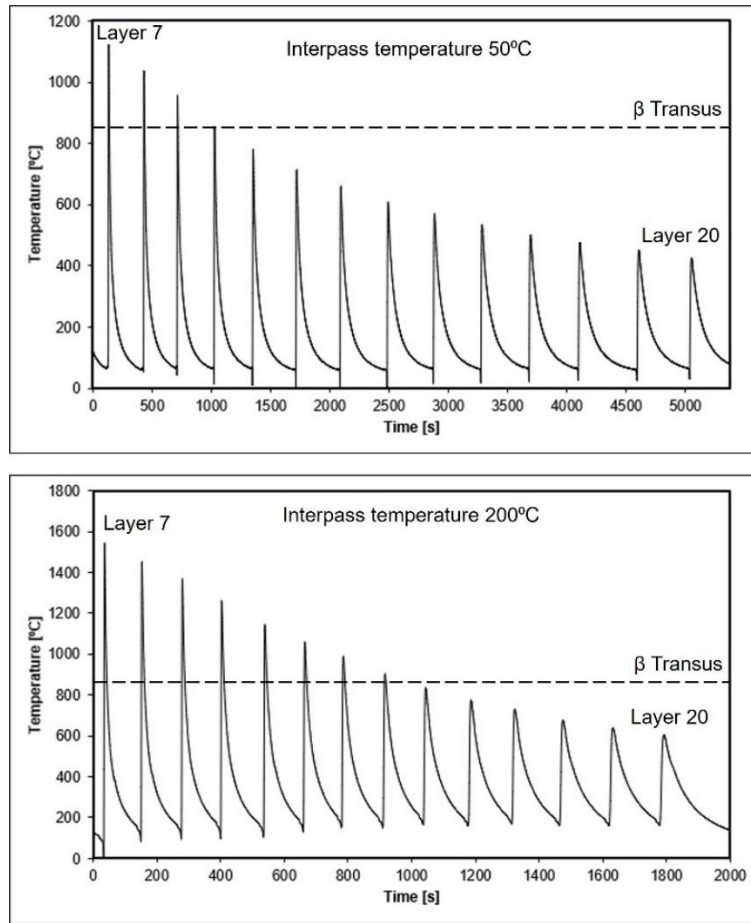


Figure 6-14. Measured thermal histories during WAAM deposition at different interpass temperatures of 50°C and 200°C.

In order to have a quantification of the cooling rate after a layer was deposited, additional data was extracted from the measured thermal histories. To measure the cooling rate, the thermal cycle corresponding to the layer 15 was selected as this is the first cycle below β transus in which the α phase can start to precipitate under the right conditions of temperature and time. Hence, this information is useful to describe the developed α laths morphology. **Figure 6-15** shows the amplified cycles corresponding to layer 15 and the measured cooling rate after reaching the peak temperature was of 3.9°C/sec, for an interpass temperature of 50°C, and 0.8°C/sec for the interpass at 200°C. These cooling rates were measured from the slopes immediately after the peak temperature was reached, as this is the critical cooling rate that will determine the characteristics of the α -phase.

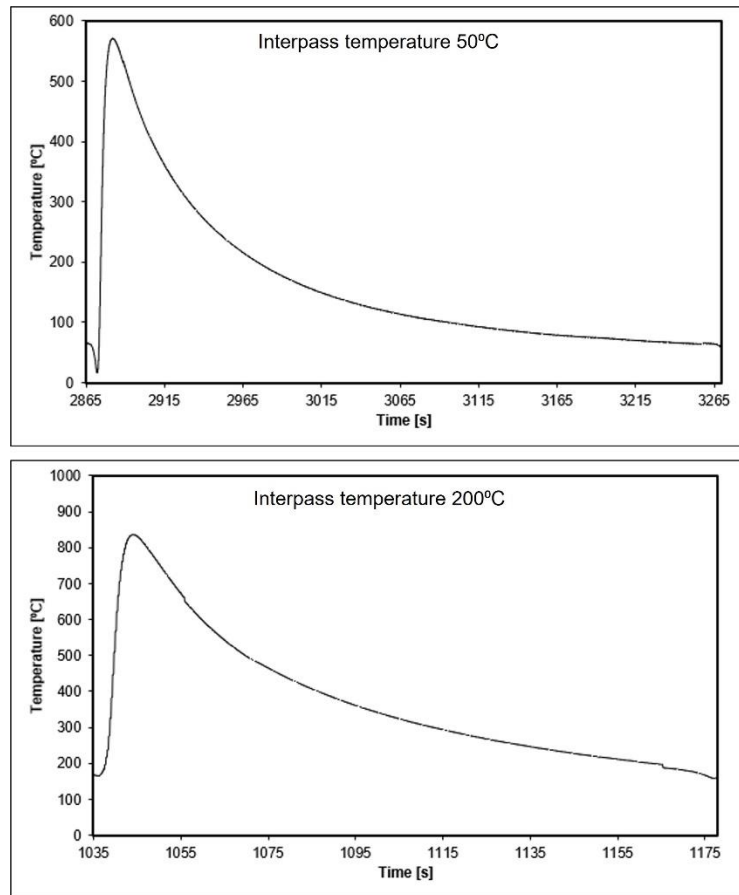


Figure 6-15. Magnification of the thermal cycles measured during WAAM deposition for the layer number 15 at different interpass temperatures of 50°C and 200°C.

6.3.5 Post-deposition heat treatment.

As shown by the previous results, during WAAM deposition of Ti-5553, coarse, columnar β grains that are strongly textured solidify during the deposition process (**Figure 6-8**). Hence, before investigating the effect of heat treatment on the mechanical properties, it was attempted as part of this work to refine to some extent the columnar grain structure. It has been previously reported for Ti-6Al-4V that a more equiaxed grain structure can be obtained by modifying the thermal conditions in the WAAM deposition process by increasing the wire feed speed to lower the G/R ratio [48]. This approach was followed and applied for the deposition of samples on single pass and oscillated pass samples. The

macrographs showing the structure of the β grain after using a higher wire feed speed are shown in **Figure 6-16**. The samples exhibited a pseudo equiaxed-columnar microstructure, as the large columnar grains are no longer obtained. Instead, some equiaxed grains and smaller grains of slight columnar morphology were achieved. This approach proved to be a feasible way to reduce the size and aspect ratio of the β grain structure on WAAM deposition of Ti-5553. This refinement of the microstructure by increasing the WFS has been attributed to two factors. First, it is suggested that the greater volume of wire provides more sites for heterogenous nucleation that can block the columnar growth. Secondly, having more wire results in a negative temperature gradient in front of the liquidus resulting in a condition less likely to promote columnar grain growth and more likely to promote equiaxed grain nucleation instead [48].

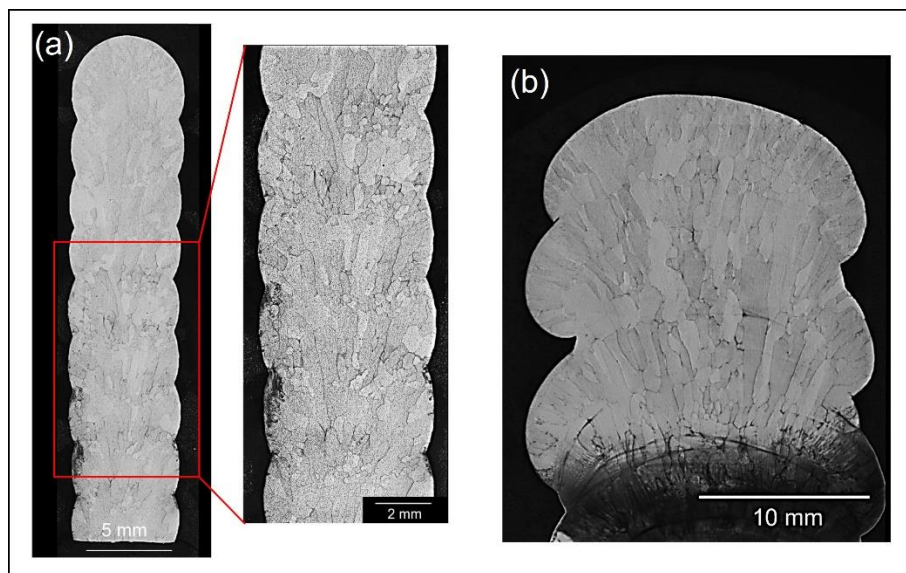


Figure 6-16. Macrographs showing the β -grain structures for the single pass and oscillated pass samples manufactured for the heat treatment investigation.

The tensile testing results before and after heat treatment of the samples built for the heat treatment investigation are presented in **Figure 6-17**. Hereafter, the single pass samples will be referred to as B1 and B2 with the suffix “ASD” and “HT”, for the as deposited and heat-treated conditions, respectively. Similarly, the oscillated pass samples will be labelled as B3-ASD and B4-HT.

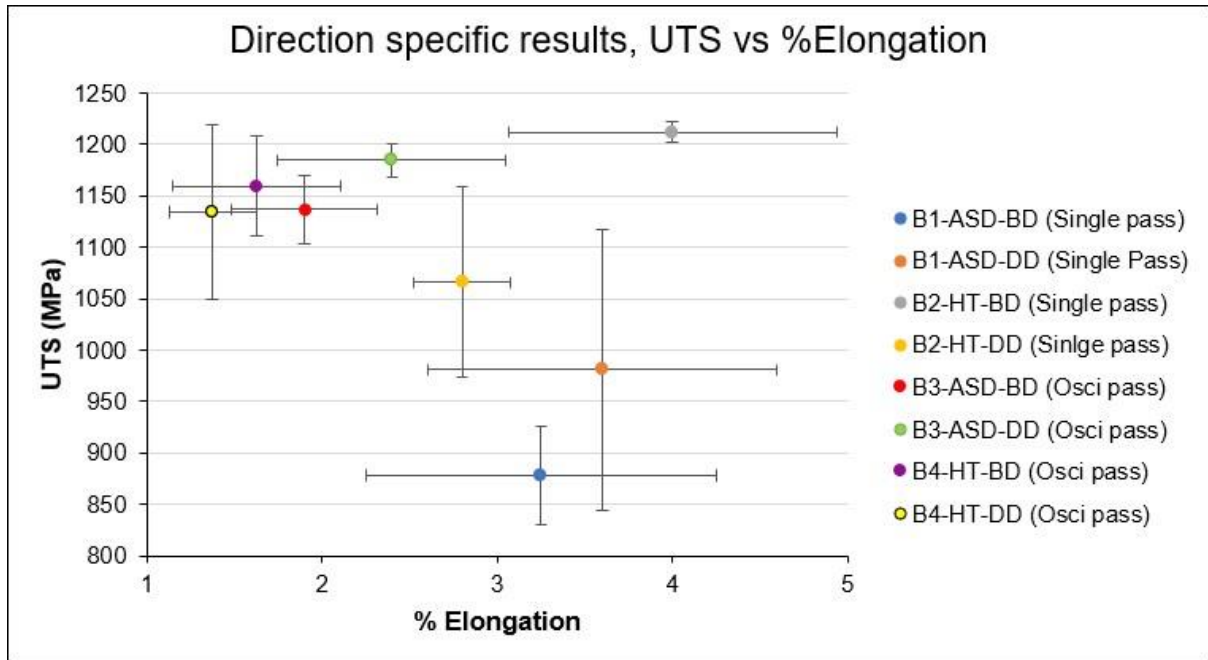


Figure 6-17. Tensile test results of samples before and after heat treatment. (BD) Building direction. (DD) Deposition direction. The error bars represent the standard deviation.

The elongation obtained during the tensile testing revealed unsatisfactory plastic performance. Samples exhibited a predominant brittle behaviour to fracture with elongation values below 4% in all cases. The oscillated samples showed lower elongation levels as compared to the single pass deposition samples. In terms of tensile strength, the values were increased after applying the heat treatment. Yield strength was not able to be quantified since no extensometer could be attached to the samples due to the premature failure of the samples. The underlying cause for this brittle behaviour was investigated in detail and it will be treated in depth in the discussion section.

The microstructure before and after heat treatment for the manufactured samples was also analysed and it is shown in **Figure 6-18** for the single pass samples, and **Figure 6-19** for the samples manufactured using an oscillated deposition path. In both the single and oscillated samples, the microstructure in terms of α phase before heat treatment is similar to the one previously described in detail in sections 6.3.2 and 6.3.3.

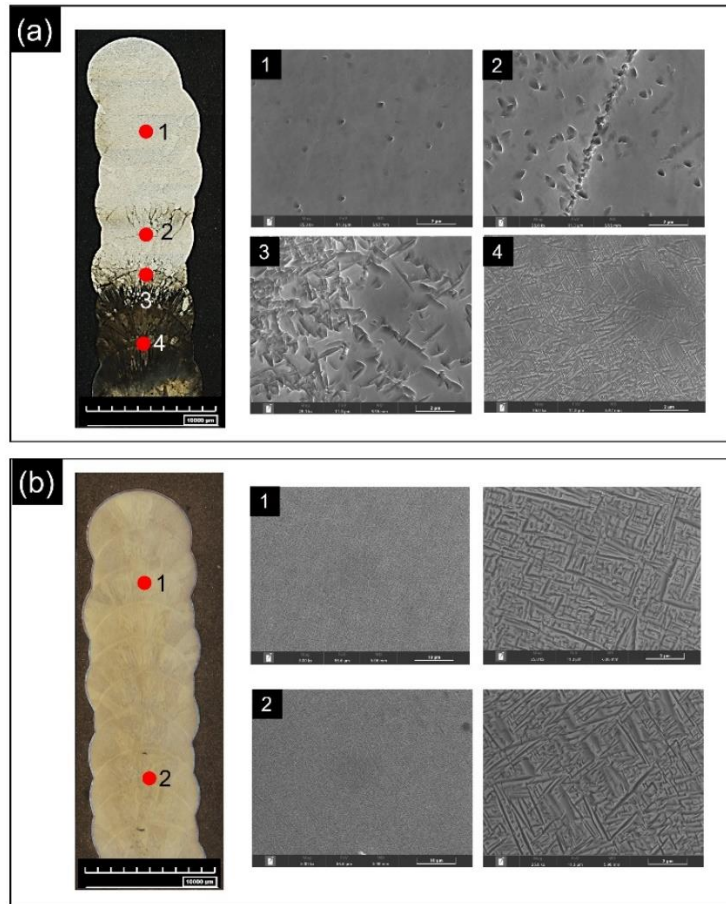


Figure 6-18. Macro and microstructures before and after heat treatment. Single pass samples: (a) Sample B1-ASD, (b) Sample B2-HT the micrographs on the right represent a higher magnification.

However, after the heat treatment has been applied, it is possible to identify that the microstructural gradients, the transition region and the microsegregation have been homogenised to produce a consistent microstructure along the build height. This is a direct consequence of the combined effect of the solution treatment that was able to dissolve back the α phase precipitated during manufacturing, in combination with the following ageing step that triggered the controlled nucleation and growth of the α phase.

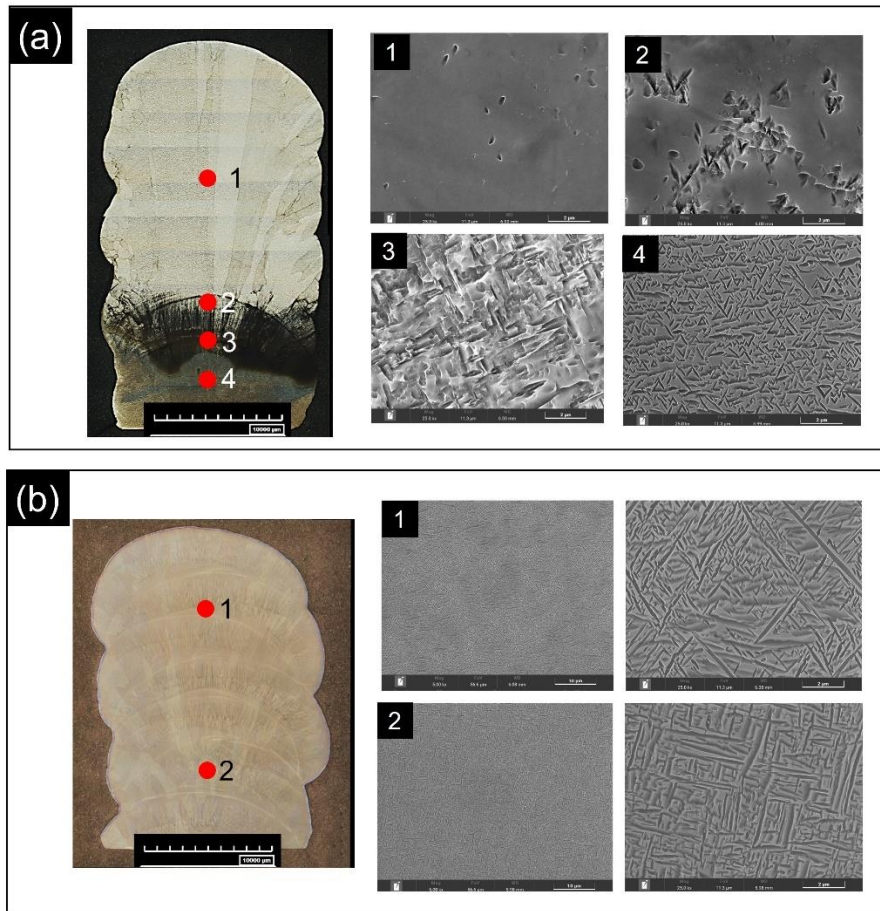


Figure 6-19. Macro and microstructures before and after heat treatment. Oscillated pass samples: (a) Sample B3-ASD, (b) Sample B4-HT the micrographs on the right represent a higher magnification.

6.4 Discussion.

6.4.1 Mechanical Performance.

Following deposition of the Ti-5553 alloy by the WAAM process using ‘standard’ build conditions, a higher proof strength was obtained compared to that reported for other as-deposited AM samples produced by higher power density processes, like laser DED and powder bed [15], [17]. The as-deposited material also had strength levels comparable with the lower end of the range possible for fully heat-treated Ti-5553 forged products [2]. Overall, this indicates that WAAM deposition naturally produced an α -precipitate microstructure in the ‘as-deposited’ state that was more similar to that found in a conventional fully heat-treated wrought component than reported for other AM processes. This high level of α precipitation generated during deposition occurred in response to the thermal cycling induced by the translated heat source, even though no attempt was made to optimise the deposition parameters to control the α microstructure, as would be normally required with a conventional wrought product.

The WAAM samples also displayed little yield stress anisotropy when measured in the orthogonal build (BD) and deposition directions (DD, **Figure 6-4**), despite the material’s strong texture (**Figure 6-8** and **Figure 6-11**) [36]–[38]. The slight variation on elastic modules can be attributed on the different volume fraction of α -phase along the height of the samples, as it is known that crystal structure is one of the variables affecting the Young’s modulus of metallic alloys [3]. However, the Ti-5553 WAAM test build solidified with a very strong $\{001\}_\beta \langle 001 \rangle_\beta$ cube texture (**Figure 6-8** and **Figure 6-11**), where two $\langle 001 \rangle_\beta$ directions are aligned parallel to both BD and DD. In addition, the α transformation microstructure formed with all 12 possible orientations determined by the BOR (**Figure 6-11**), which would lead to a similar Taylor factor in each loading direction [39]; so, if *only* the effect of texture is considered, both the BD and DD tensile test directions will be similar due to cube symmetry. The tensile tests did, however, display significant anisotropy in their elongation (as have other Ti-5553 AM samples [15]) where the build direction exhibited less than half the ductility of the DD samples. Anisotropy in tensile ductility is regularly reported for Ti-64 WAAM components

[36]–[38], and has been attributed to a heterogeneous distribution of ‘hard’ and ‘soft’ microtexture regions present in the α transformation microstructure, associated with the coarse columnar parent β -grain structure, which causes severe shear concentration at the β -grain boundaries during transverse loading [40]. The fracture behaviour of the current Ti-5553 WAAM samples was not investigated, but given the preferential nucleation of α on the β -grain boundaries (e.g. **Figure 6-7b-c**), and the presence of large, columnar β -grains present in the tensile test samples (**Figure 6-8**), the low elongation to failure in DD is similarly probably a consequence of shear concentration in the region of the aligned columnar β -grain boundaries.

6.4.2 Solidification Microstructure.

Coarse and columnar β -grain structures that exhibit strong $\langle 001 \rangle_{\beta}$ fibre textures are commonly observed in titanium alloys produced by WAAM, particularly in Ti-64 components [18], [40]–[42]. This grain structure is a consequence of the positive thermal gradient in the liquid at a solidification front in a heated melt pool, combined with both a lack of nucleation sites in the melt pool and low solute partitioning, which during solidification leads to low constitutional supercooling. The primary β -phase solidification behaviour is consequently dominated by epitaxial growth from the fusion boundary without significant nucleation ahead of the solidification front [43]–[45]. As Ti-5553 contains alloying elements that produce greater solute partitioning during solidification than Ti-64 (Mo, $k = 2.0$; Cr, $k = 0.81$; Fe, $k = 0.79$ [9]–[11], [34]), the coarse and columnar solidification structure seen in **Figure 6-6** and **Figure 6-8** was not a foregone conclusion. Schiel-Gulliver solidification calculations produced with the JMatPro thermodynamic modelling software [46] in **Figure 6-20a** also highlight the difference in microsegregation trends between Ti-5553 and Ti-64. These plots show the predicted segregation of Cr and Fe and the inverse segregation of Mo across a dendrite, which will result in local variation in the β -phase stability across the solidified microstructure. In addition, an EPMA line scan across two prior dendrite cores from near the top of the Ti-5553 wall has been included in **Figure 6-20b** (the line scan area is indicated in **Figure 6-9b**). In general, the trends

match the modelling results; i.e. Mo partitioning is observed towards the dendrite cores and Cr and Fe to the interdendritic regions, with minimal segregation of Al and V to the core and dendrite boundaries, respectively.

The EPMA maps further confirmed the presence of a solute segregation band at the fusion boundary for each melt track (**Figure 6-9a**), which were identified in the optical macrographs in **Figure 6-6** from the etching contrast. These fusion boundaries etch lines have previously been attributed to the transient partitioning of solute that develops due to the melting back and acceleration of the solidification front that occurs at the edge of the melt pool as the heat source is translated [22]. This results in fusion-boundary bands rich in Mo, but lean in Cr and Fe, which can be conveniently used to identify the convex melt pool depth profile seen in the BD-TD sections in **Figure 6-6**.

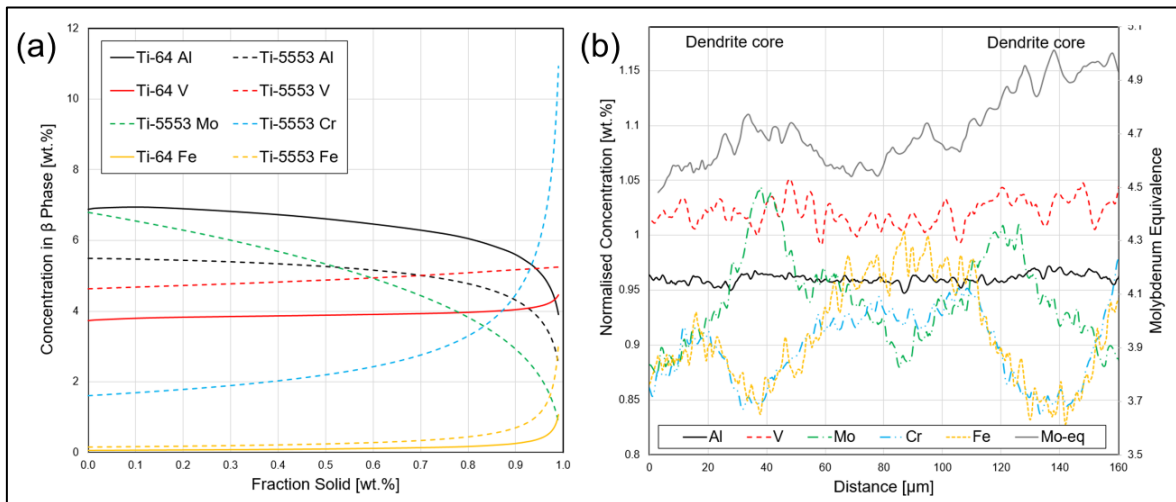


Figure 6-20. Microsegregation across a dendrite: (a) predicted by JMatPro Scheil solidification calculations for Ti-5553 and Ti-64 compared to (b) smoothed EPMA line scan data in TD from the region highlighted in Fig. 6-8b, averaged in BD, across two dendrite cores in the top of the Ti-5553 WAAM wall. The molybdenum equivalence (Mo-eq) has also been calculated from the EPMA compositional data and added to (b) to show the variance in β -phase stability.

Even though more significant solute segregation was found in the Ti-5553 WAAM samples compared to in Ti-64, the β -grain structure still exhibited coarse, columnar grains (**Figure 6-8**) as well as a strong $\langle 001 \rangle_{\beta}$ texture. The additional

constitutional cooling possible in Ti-5553 due to its different alloy constitution was therefore still insufficient to promote nucleation ahead of the solidification front, with the standard WAAM process conditions employed. Nevertheless, the presence of a surface skin of finer grains (**Figure 6-8**), which is not normally seen with a Ti64 alloy using the same processing parameters (e.g. [18]), is indicative of a higher degree of constitutional supercooling with Ti-5553. This change in surface grain structure requires further investigation, but is related to the curvature of the solidification front seen in the transverse sections that would require dendrites with a $\langle 001 \rangle_{\beta}$ // BD orientated grain to grow at $\sim 45^\circ$ to BD to follow the thermal gradient close to the wall surfaces (**Figure 6-6**). Greater solute partitioning resulting in a wider mushy zone would thus give more opportunity for dendrites to reorientate closer to their preferred crystallographic growth direction, with respect to the solidification front, by dendrite fragmentation or other mechanisms [47]. Some small discrete equiaxed β grains were also observed to be present in the core of the wall that were engulfed by the more favourably $\langle 001 \rangle_{\beta}$ // BD orientated columnar grains (**Figure 6-8**). These findings thus show greater potential for the Ti-5553 alloy, compared to Ti-64, for forming a more equiaxed grain structure by modifying the thermal conditions in the WAAM deposition process (for example, by increasing the wire feed speed to lower the G/R ratio [48]). It is for this reason that this approach was implemented in this work as an attempt to refine the β grain structure before the post deposition heat treatment investigations were performed.

6.4.3 α -Phase Precipitation.

During conventional solution heat treatment of Ti-5553, cooling rates from above the β transus faster than 0.1°C/s prevent precipitation of the α phase [32]. The subsequent decomposition of the metastable- β phase during sub-transus ageing treatments is complex and can occur through multiple pathways, which include the formation of the athermal ω phase by a diffusionless transformation, spinodal decomposition, and the development of ordered and disordered forms of O' and O'' [6], [7], [49]–[51], all of which are transition states that can affect the subsequent nucleation of the α phase during ageing heat treatments. The solvus

temperatures of these metastable precursor phases are relatively low (<400 °C) and to form they generally require far longer heat treatments and lower heating rates than are experienced during a typical WAAM thermal history. However, more recent publications have also claimed, based on evidence from step-quenching experiments, that a pseudo-spinodal mechanism may allow the α phase to nucleate directly from β , at higher temperatures during short isothermal ageing times (<15 minutes), in the temperature range of 600 – 700 °C [6], which coincide with the nose of the α time-temperature-transformation curve [32]. This proposed mechanism has been reported to generate both a high density and homogeneous distribution of α -lath precipitates, without the requirement for heterogeneous nucleation sites, such as dislocations or metastable precursor precipitates like the ω phase [6], [49].

In the WAAM process, after solidification, a dynamic local volume of material is reheated multiple times with a diminishing peak temperature rise as the heat source travels across the surface when each new layer is added (**Figure 6-5**). For the experimental conditions used in this work, the measured cooling rate during the first WAAM heating cycle was around 60 °C/s (**Figure 6-5**), higher than that required to prevent α formation during cooling in Ti-5553 [32], [52]. The regions of the build that are reheated in excess of the β transus temperature, but are located high enough in the build that they are not further reheated below the β transus, would, therefore, be expected to remain as a metastable- β phase on cooling to room temperature. Consequently, no α precipitates were observed in the top 9 layers of the build. This behaviour would then persist to a depth where the peak temperature reached on reheating, caused by the thermal field of the translated heat source, became lower than the β -transus temperature, but where the temperature rise was still sufficient for the α transformation kinetics to allow precipitation in a short enough time; i.e. the accumulative time spent above 600 °C in cycles 9 - 11 is typically less than 100 seconds (**Figure 6-5**).

This precipitation evolution throughout the build can be tracked using Vickers hardness mapping, and a map of the top 24 layers of the build and a line profile across them have been provided in **Figure 6-21**. In the top β -annealed section of

the wall, where there is no α precipitation, the hardness is at a minimum of ~320 HV (0 – 14 mm below the top surface of the build, **Figure 6-21b**). As the α begins to precipitate in the transition region (~14 – 20 mm in **Figure 6-21b**), the hardness begins to increase, until reaching an average peak hardness of ~500 HV in the dark-etched lower section of the build (>22 mm), which is representative of the bulk. When compared to other Ti-5553 deposits in the literature, the WAAM bulk ‘as-deposited’ hardness is higher than other as-deposited AM builds and their aged counterparts (e.g., [4], [27]). This provides further credence that the WAAM thermal history intrinsically produces highly efficient α precipitation that results in a high density of fine α laths.

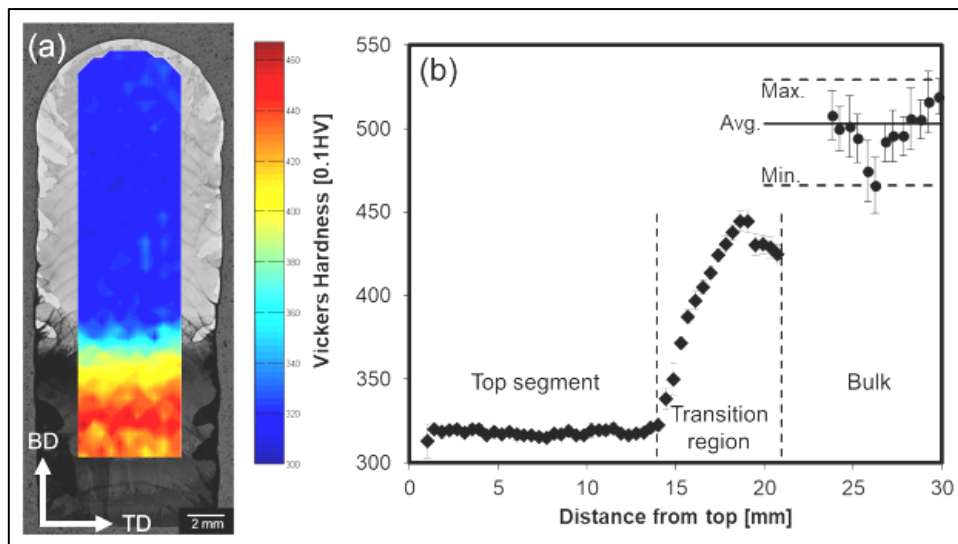


Figure 6-21. Microhardness distribution of the upper Ti-5553 WAAM sample section, showing: (a) a hardness map superimposed on an optical image and (b) a hardness-line profile produced from the hardness map using values averaged across 13 measurements in TD.

From the ‘harpoon’ thermal measurements, it can be seen that the homogenised alloy’s β transus temperature of 850 °C would be expected to equate to about the top 8-9 layers, although the transition region where the hardness started to increase (**Figure 6-21**) and α precipitation was first seen occurred below approximately layer 12, where the measured peak temperature rise had fallen to <700 °C (or ~150 °C below the β transus). By the ~15th layer, where the α -lath volume fraction stabilised (**Figure 6-10**), and the hardness then reached a

maximum level (**Figure 6-21**), the peak temperature was measured to have dropped further to ~650 °C. However, it should be noted that the harpoon method only measures the temperature history at a single location, and due to the thermal gradient under the heat source, it is not possible to extract the exact temperature rise at which α precipitation initiates. In addition, the microsegregation noted above will affect the stability of the β phase and the local transus temperature. The main α -phase stabilising element Al ($k = \sim 1$ [11], [35]) marginally segregated inversely (**Figure 6-9b**), in a similar direction to Mo; however, the amount of segregation was minimal compared to Mo [8], [9], which is a strong β -phase stabilising element in Ti [1], [3]. The other β -stabilising elements, Cr and Fe, became concentrated in the interdendritic regions [10], [11]. An approximate calculation of the overall effect this would have on the relative change in β -phase stability using the Mo-equivalence index (Mo_{eq}) in Ref. [1], gives a maximum of $Mo_{eq} \approx 5.0$ for the dendrite cores and $Mo_{eq} \approx 4.6$ for the interdendritic regions. These estimates represent the maximum possible influence of segregation on the parent β -phase stability, as back diffusion and repeated re-heating above the β transus will tend to reduce solute gradients after solidification. For example, there is some evidence of the Fe distribution, which has a high diffusivity in β [3], homogenizing with depth in the build.

As a consequence of the solute segregation pattern after solidification, after the 12th heating cycle, α can be seen in the optical micrograph of the Ti-5553 WAAM deposit shown in **Figure 6-7** to begin to first nucleate heterogeneously within the β grains and at the β -grain boundaries (**Figure 6-7b-c**), which are sites favoured for α nucleation at low undercoolings [53], [54]. Earlier nucleation of coarser α laths was also seen within the β grains (**Figure 6-7d**) with a distribution similar to the dendritic segregation pattern that occurred during solidification. In the following heating cycles, as the peak temperature falls and the undercooling increases, precipitation of finer α laths can be seen to expand within the remaining β matrix until after the 15th heating cycle, where the microstructure had been reheated multiple times and the peak temperature had dropped to ~650°C, and they cover entire β grains. This suggests that these finer homogeneously distributed laths are nucleated during a heating cycle that hits a narrow range

corresponding to the 'nose' of the nucleation curve, which is known to lie between 600 – 800 °C [32]. However, the fact that they precipitate within such a short accumulative time at temperature and with a very rapid heating rate suggests their nucleation pathway is consistent with the pseudo-spinodal mechanism proposed by Nag *et al.* [6], [55], whereby a fine-scale microstructure can be produced in a short time without any apparent prior heterogeneous nucleation sites in the β matrix. However, an independent study utilising controlled rapid heating experiments, with comparison to the results in refs. [6], [55], would be required to verify this precipitation sequence.

Overall, the finer and homogeneously distributed α laths seen within the dendrite cores form the majority of the final transformation microstructure (e.g. **Figure 6-11**) and are similar to those found in a classically solution treated and aged Ti-5553 microstructure [3], [4], [31], [56], [57]. Their high coverage of the parent β grains, combined with the high volume fraction estimated for the α -phase precipitates from **Figure 6-11**, is consistent with the comparable proof stress levels measured in the tensile tests. However, fortunately, for Ti-5553 WAAM components, due to their low quench sensitivity, it is also viable to conduct post-deposition β -solutionizing and conventional ageing heat treatments to precipitate a tailored α microstructure even more homogeneously, throughout an entire part, to optimise the mechanical properties for a target application [2], [15], [27], [31].

6.4.4 Influence of different thermal cycles on microstructural evolution.

Changing the inter pass temperature during WAAM deposition produced different thermal histories which influenced the microstructure. The α phase precipitation sequence and mechanism were the same as explained in the previous section. However, these experiments further revealed that the α phase evolution is closely dependent on the thermal cycles introduced. In the case of the lower interpass temperature of 50°C, the higher volume of α phase fraction observed is a consequence of the lower dwelling temperature below the β transus temperature which allows less dissolution of alpha as more cycles were added. Conversely, since the sample with an interpass temperature of 200°C experienced a higher

number of cycles above the α phase stability temperature, this caused a reduction in the volume fraction of this phase in the final developed microstructure. The faster cooling rates during the interpass temperature of 50°C also helped to restrict the growth of the α laths once they were formed by slowing down the diffusion rates, producing finer features than the ones observed for an interlayer temperature of 200°C. The results discussed so far have shown that significant microsegregation and microstructural gradients form due to the repetitive heating and cooling cycles inherent to the WAAM process. For this reason, it becomes evident the need to apply a post-deposition heat treatment to homogenise the microstructure and optimise the mechanical properties.

6.4.5 Effect of post-deposition heat treatment on microstructure and mechanical properties.

The samples manufactured for the heat treatment investigation with a pseudo columnar-equiaxed microstructure (**Figure 6-16**) showed an unexpected brittle behaviour as compared to the elongation results obtained in **Table 6-1**, even after the heat treatment was applied. The main difference between these two sets of samples was that the samples manufactured to study the effect of post-deposition heat treatment were manufactured by feeding two wires simultaneously in order to increase the wire feed speed as a way to refine the β -grain structure. Hence, the β -grains morphology has significant differences in terms of size and aspect ratios between these two sample conditions. For the samples with high wire feed speed, the grain size was decreased and a mix of columnar and equiaxed grain was obtained (**Figure 6-16**). This also generated a higher fraction of grain boundaries as compared to the sample presented in **Figure 6-8**. It is known that the nature of the grain boundaries can have an important effect on the plastic behaviour of titanium alloys [3]. The near β alloy Ti-5553, both in the as deposited and heat-treated condition, is formed by both α and β phase. The α -phase is HCP, which has limited slip systems as it is characterised by high strength and low plastic deformation. On the other hand, the β -phase is BCC and undergoes plastic deformation much more readily than the α -phase. Continuous α -phase unavoidably forms along prior- β grain boundaries in Ti-5553 thermal processing and it is known as grain boundary α (GB α). Coarsening of GB α is a diffusion-

controlled growth process involving the rejection of β stabilising solutes into the β matrix. This creates a precipitates free zone (PFZ) adjacent to the GB α . Strain incompatibility at this interface between α and β can lead to void nucleation and easy crack growth and local initiation of microcracks [15]. Premature fracture can take place due to microvoids nucleation and coalescence at grain boundaries. Hence, by refining the β -grain structure, the susceptibility to failure by this mechanism could have been increased as a consequence of the higher fraction of grain boundaries throughout the sample.

Based on the aforementioned mechanism, it can be hypothesised that the implementation of two wires feeding led to the refinement of the prior β grains to some extent. This introduced a higher fraction of grain boundaries in which GB α can form. This translated into a higher number of regions with PFZ which served as nucleation sites for voids coalescence and microcracks that caused premature failure. To verify this hypothesis, fractographic and microstructural analysis was carried out on selected tensile coupons. A correlation between grain morphology and fracture surface characteristics was established. To do this, one half of the tensile coupon was sectioned along the axial plane of the tensile coupon to check the microstructure adjacent to the fracture. Then, a section perpendicular to the axis of the coupon was extracted to perform the fractographic analysis. **Figure 6-22** shows an amplified region adjacent to the fractured path of a coupon extracted from B3-ASD in the DD direction and with an elongation value of 2%. It is clear that detachment at the grain boundaries has taken place as a consequence of the applied stress during tensile testing. The tortuous patch of the crack profile also suggests that intergranular cracking took place causing the premature failure of the samples.

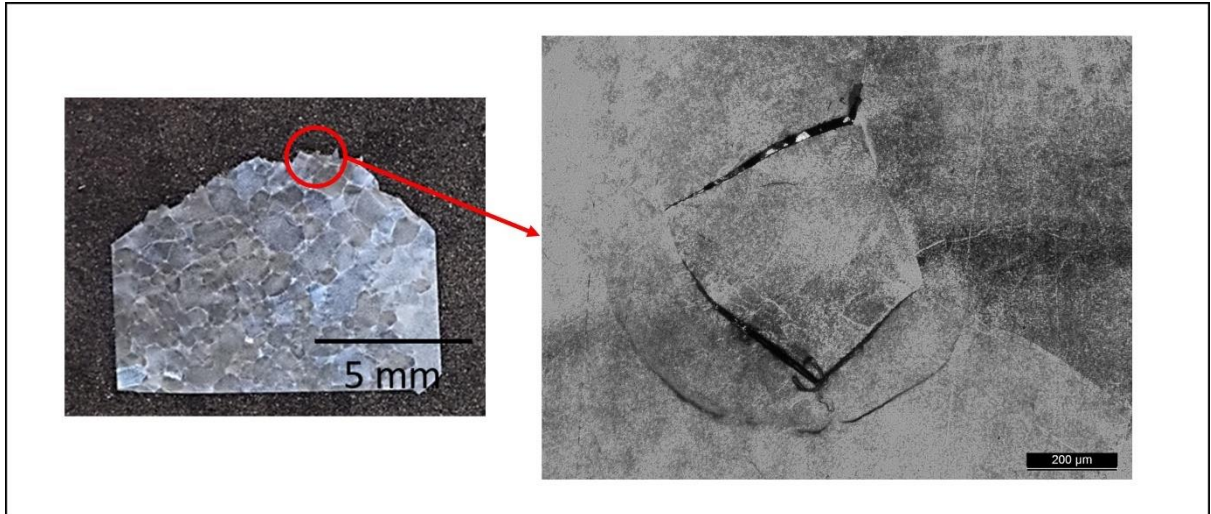


Figure 6-22. Magnification at the fracture region of tensile coupon extracted from B3-ASD (oscillated pass sample) showing intergranular cracking.

Additional imaging on other adjacent locations of the same sample shows very clearly that cracks originated at the grain boundaries (intergranular cracking) and then propagate to the bulk of the grain (transgranular cracking) producing a mixed fracture mode (**Figure 6-23**). These observations highlight the crack initiation mechanism and support the suggested hypothesis for the poor plastic performance of the samples.

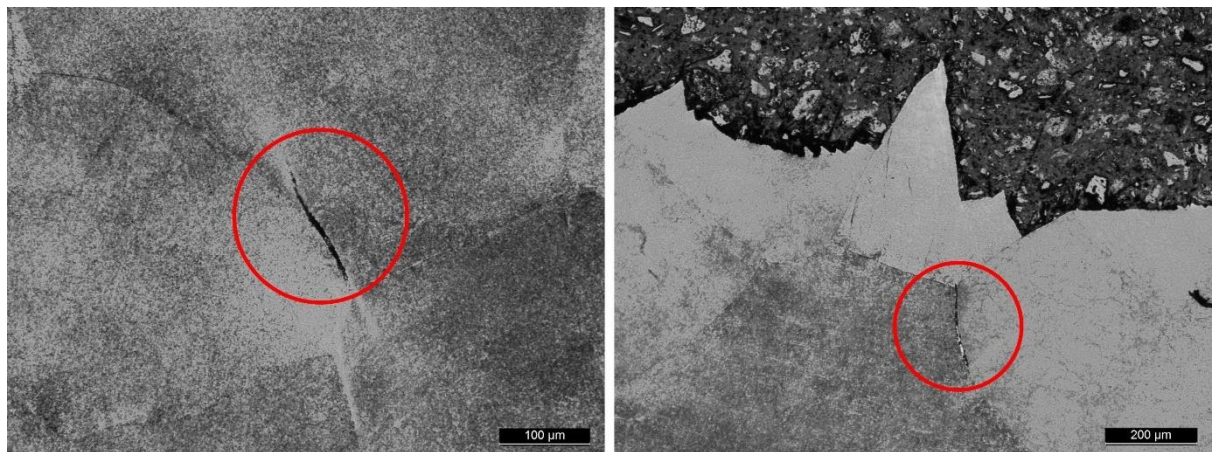


Figure 6-23. Optical microscopy of other areas adjacent to the fracture surface of tensile coupon extracted from B3-ASD showing how cracks are generated at the grain boundaries and then propagate within the grains.

The fractographic analysis presented in **Figure 6-24**, for the same B3-ASD sample, clearly reveals a mixed intergranular-transgranular fracture mode where microvoids coalesce and cracking take place at the grain boundaries and then propagates within the grain as shown in **Figure 6-23**. Transgranular fracture features can be easily identified as the α lamellar pattern is revealed when the crack goes across the grains.

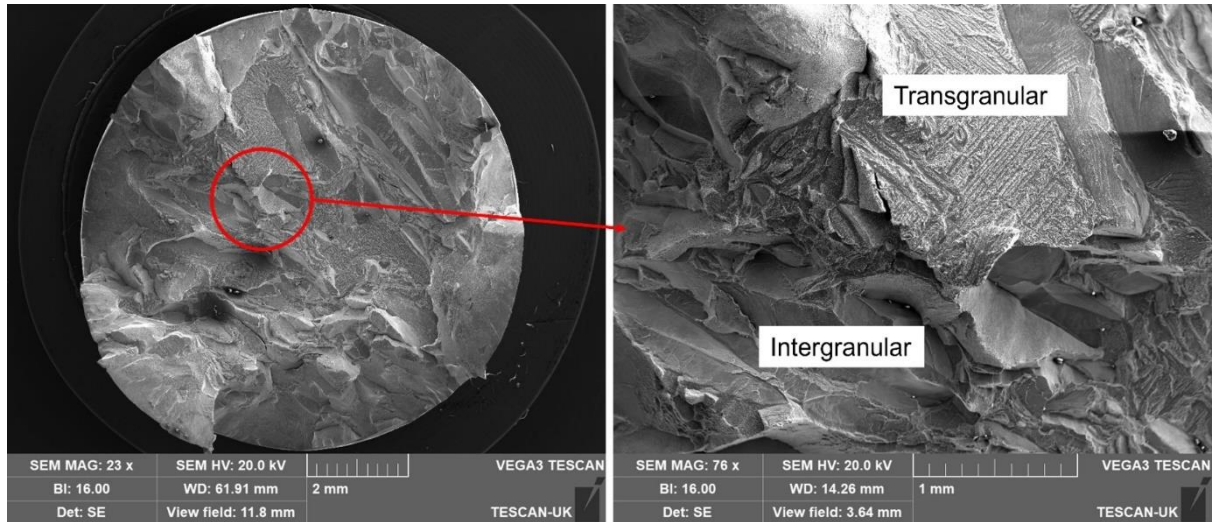


Figure 6-24. SEM fractographic imaging of sample B3-ASD showing the mixed intergranular-transgranular fracture mode.

Figure 6-25 (right) also shows the magnification of an intergranular cracking feature that reveals dimples on the surface of the grain. This is evidence of the presence of soft PFZ close to the GB α that can readily deform plastically. Additionally, the small size of the dimples in this region also suggests that the plastic zone was constrained geometrically by the adjacent grain boundary region.

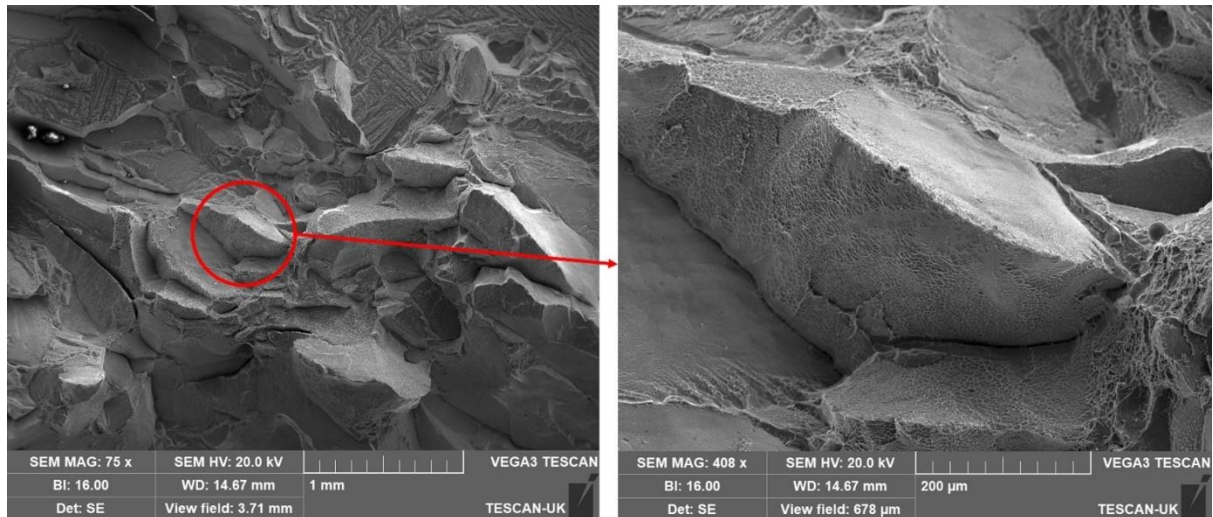


Figure 6-25. SEM fractographic imaging of Sample B3-ASD-L3 showing the features on the surface on an intergranular crack.

To further verify the presence of GB α and PFZ, SEM imaging of the microstructure from a sample taken from B2-HT (single pass sample with lower elongation) was performed. It was possible to identify the GB α that generates PFZ banding in the adjacencies (**Figure 6-26**). The GB α thickness is $\sim 0.6\mu\text{m}$ in this region. As previously explained, during the WAAM deposition process, the α phase begins to first nucleate heterogeneously within the β grains and at the β -grain boundaries, which creates the right conditions for the formation of GB α . Additionally, even though it would be expected that most of the α phase is dissolved back into solid solution during the solutionising step of the post-deposition heat treatment, if the cooling rates are slow enough after this step, then GB α can also form. The measured cooling rate after the solution step performed in this work was around $0.15\text{ }^{\circ}\text{C}/\text{sec}$, which is close to the $0.1\text{ }^{\circ}\text{C}/\text{sec}$ threshold to prevent precipitation of the α phase [32]. Hence, suitable conditions were produced to form GB α . This shows that if the formation of GB α wants to be minimised, the heat treatment needs to be carefully controlled and optimised to keep as low as possible the formation of this detrimental phase for the plastic performance of WAAM Ti-5553 components.

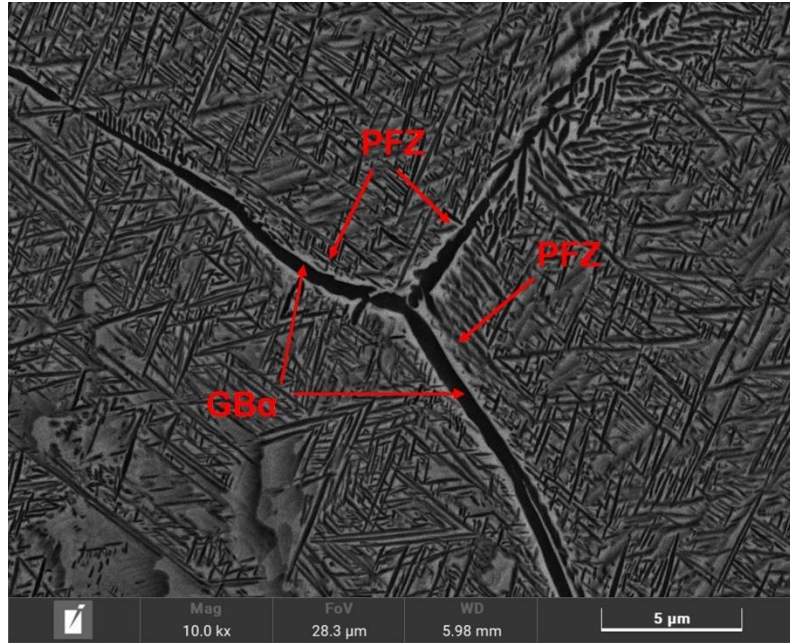


Figure 6-26. SEM image showing the PFZ on a grain boundary triple point. Sample B2-HT.

Since the PFZ formation is a consequence of the rejection of β stabilising element from the grain boundaries, enrichment of these elements can be expected in this region. A SEM-EDS linear scan along a GB α allowed to quantify the variance of the alloy elements concentrations (**Figure 6-27**). It is possible to see how the GB α has a higher concentration of Al as expected, while the PFZ is richer in β -phase stabilising elements Mo, V and Cr. This helps to further verify the presence of PFZ at the grain boundary locations.

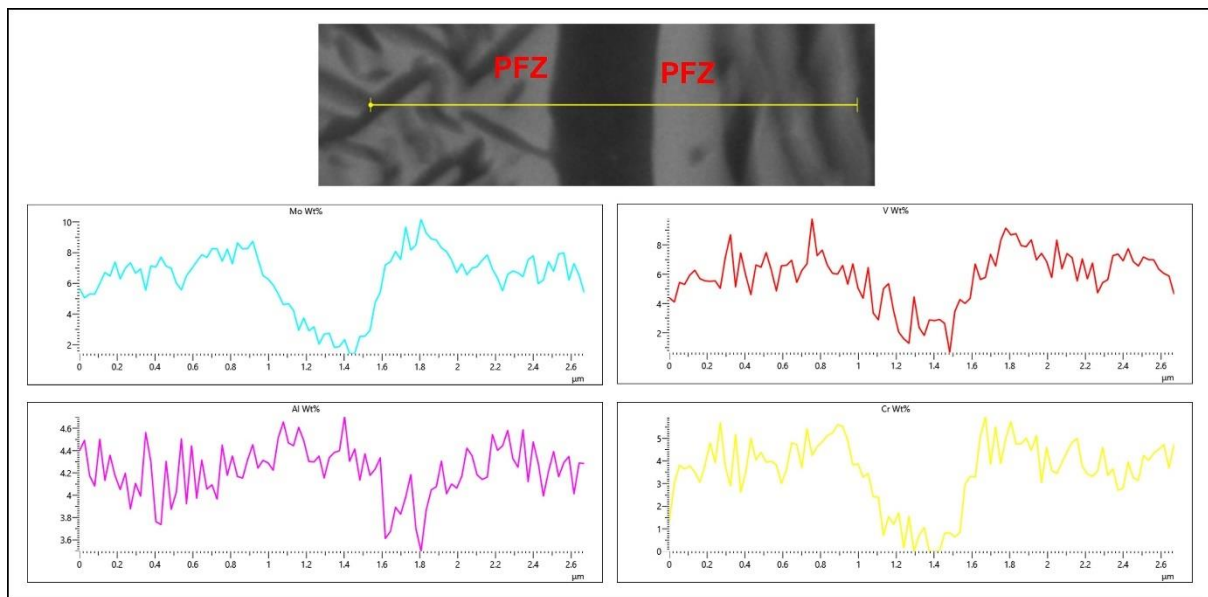


Figure 6-27. Linear SEM-EDS concentration scan along a GB α and PFZ showing the local concentration of α and β stabilising elements. Sample B2-HT.

From Figure 6-17, oscillated pass samples exhibited lower elongation values as compared to the single pass samples. As can be seen in **Figure 6-28**, the GB α found in the samples built with an oscillated deposition strategy (B4-HT) is thicker as compared to the samples manufactured using a single pass deposition (B2-HT). This is a consequence of the inherent higher heat accumulation during the oscillated strategy due to the longer dwelling time of the plasma heat source in specific volume regions of the build. Since GB α formation is a diffusion process, dwellings at a higher temperature for a longer time led to thicker features in the oscillated samples. In this case, GB α has a thickness of $\sim 1.11\mu\text{m}$ and $\sim 0.7\mu\text{m}$ for the oscillate and single pass samples, respectively.

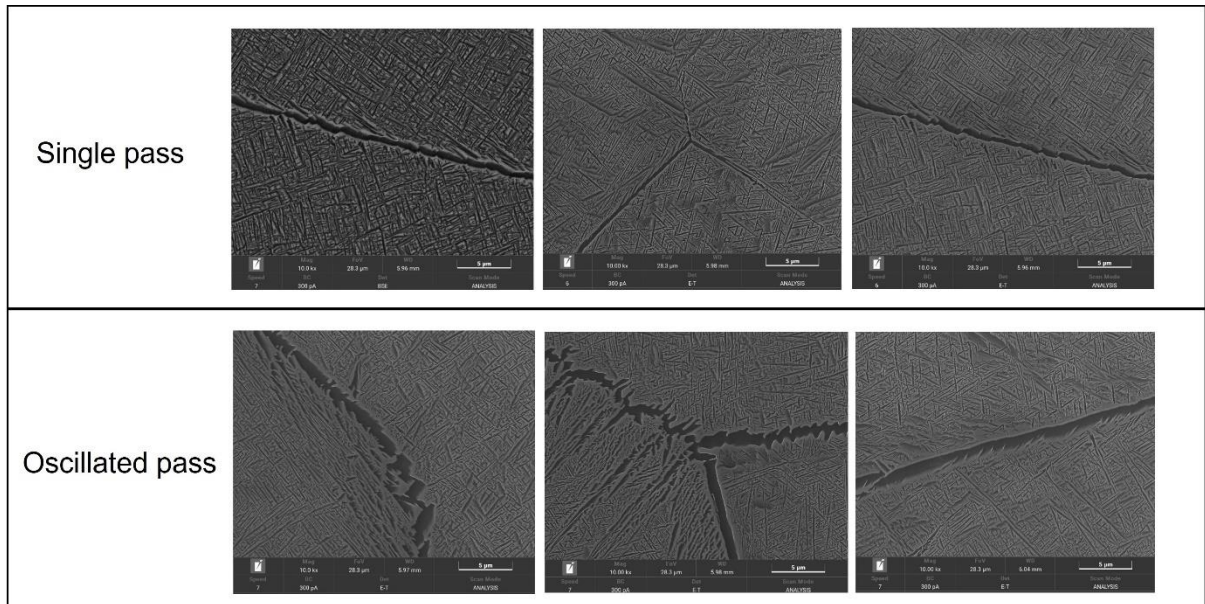


Figure 6-28. Comparison of the GB α and PFZ between single and oscillated deposition strategies showing coarser features for the oscillates pass samples. Single pass sample B2-HT. Oscillated pass sample B4-HT.

Even though it has been reported that GB α cannot be avoided completely during the industrial processing of Ti-5553, it can be suggested that the microstructure obtained during WAAM is particularly susceptible to the embrittlement mechanism described due to the fully lamellar nature of the WAAM microstructure. In contrast, Ti-5553 components manufactured by “traditional” methods, such as forging, have a bimodal microstructure (Error! Reference source not found.) where the mixture of equiaxed α grains and laths can contribute to a better distribution of the strain when stress is applied helping to reduce the likelihood of microcracks nucleation and coalescence at the GB α /PFZ interfaces. It has been shown that refining the β grain structure of WAAM deposited Ti-5553 can lead to poor brittle performance of the component due to the growth of GB α and formation of PFZ as a consequence of a higher fraction of grain boundaries when the β grains are refined. The heat treatment applied in this work proved to be unsuccessful in minimising these phases and tailored heat treatments should be developed in future work if the properties of WAAM Ti-5553 want to be optimised.

6.5 Conclusions.

The microstructural evolution during WAAM processing of the near- β alloy Ti-5553 has been investigated for the first time. Correlation to the solidification microstructure that creates the parent metastable β phase prior to the precipitation of α , the complex cyclic temperature history in the WAAM process and the study of the effect of post-deposition heat treatment on the microstructure and mechanical properties, has revealed the following main conclusions:

- The tensile strength of the 'as-deposited' WAAM Ti-5553 build was superior to that reported for other higher energy density AM processes, due to the high density of α precipitation produced by cyclical heating when using a more diffuse plasma-arc heat source.
- β -phase EBSD orientation maps showed that, with the deposition conditions investigated, the WAAM Ti-5553 build developed a coarse and columnar β -grain structure, with a strong $\{001\}_{\beta}\langle 001 \rangle_{\beta}$ texture, which resulted in anisotropic elongation during tensile testing.
- The greater solute partitioning seen in the Ti-5553 alloy, compared to in Ti-64, was still not able to promote an equiaxed β -grain structure in the bulk of the sample under standard WAAM conditions. However, it was found that, where the curvature of the solidification front caused a large deviation from the preferred $\langle 001 \rangle_{\beta}$ dendrite growth direction, the wider mushy zone was sufficient to cause a skin layer of smaller new grains to develop at the surfaces of the build with a growth direction tilted away from the build-height direction.
- EPMA chemical maps revealed that significant solute microsegregation occurred during solidification, with Mo and Al partitioning to the dendrite cores, and Cr, V, and Fe to the dendrite boundaries. Repeated thermal cycling during deposition did not remove this solute segregation completely.
- Due to the low quench sensitivity of Ti-5553, α precipitation did not occur on cooling through the β transus, but a high density of α laths were found

to start to precipitate during reheating in subsequent thermal cycles when the peak temperature fell below $\sim 700^{\circ}\text{C}$. This initiated heterogeneously with α precipitating first in interdendritic regions and at β -grain boundaries, where the lower local Mo concentration reduced the stability of the parent solid solution. A high density of finer laths was then observed to form uniformly within the remaining matrix as the peak temperature reduced, and precipitation was complete when the peak temperature in subsequent reheating cycles fell below 600°C . The relatively short time available for nucleation and homogeneous distribution of the precipitates suggests this may have occurred by the 'pseudo-spinodal' mechanism proposed in refs. [6], [55].

- The high density of α precipitation during the WAAM process produced a material strength comparable to the lower end of the range reported for fully heat-treated wrought Ti-5553 products.
- Different thermal cycling during the deposition process has an important influence on the final developed as deposited microstructure of WAAM Ti-5553. This accentuates the need for tailored post-deposition heat treatments that can control and homogenise the α phase distribution producing isotropic material properties.
- Refining the β grain structure increased the fraction of brittle phases ($\text{GB}\alpha$) and PFZ formed at the grain boundaries that caused a poor plastic performance of the components. Evidence showed that post-deposition heat treatment needs to be optimised in order to minimise these features and increase elongation.

6.6 References.

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7 Effect of initial feedstock chemical composition on tensile properties of Ti-6Al-4V produced by Wire and Arc Additive Manufacture.

This chapter is based on the following paper draft that is planned for submission in the Journal of Materials Processing Technology.

A. Caballero, J. Ding, S. Williams. *Effect of initial chemical composition on tensile properties of Ti-6Al-4V produced by Wire and Arc Additive Manufacturing*. Paper draft planned for submission in the Journal of Materials Processing Technology.

The final chapter of this work is dedicated to the evaluation of the embrittlement of Ti-6Al-4V due to the varying content of interstitial elements on the material feedstock used during WAAM. This is one of the main concerns involved while fusing titanium and it is not clear in industrial practice what the actual limits for interstitials concentrations are. A systematic study was performed by increasing the interstitials content on the wire feedstock used. The microstructural features developed during WAAM Ti-6Al-4V proved to have a good tolerance for the dilution of oxygen without compromising the plasticity for higher concentrations than the ones established by the relevant standards. Additionally, the results showed a potential way to increase the strength of the material by changing the wire composition.

Abstract: Interstitial elements such as oxygen and nitrogen have a large effect on the mechanical properties of Ti-6Al-4V. The aim of this work was to study the influence of the chemical composition of the wire feedstock on tensile properties of Ti-6Al-4V manufactured by Wire and Arc Additive Manufacture (WAAM). Samples manufactured by WAAM using a single pass deposition strategy were produced using different wires with increasing content of interstitial elements. The rest of the deposition parameters were kept constant for each of the samples tested. Tensile coupons were machined from the deposited samples and the tensile properties were tested. Microstructural, chemical, and fractographic analyses were also performed. It was found that the proof strength and ultimate tensile strength of the deposits increase linearly as a function of the oxygen

equivalent of the wire feedstock. In addition, tensile ductility was not compromised for higher interstitial element contents. No significant difference in microstructural features was found between the analysed samples and similar values for the α lamella thickness were measured. Hence, the higher strength found for the samples with higher oxygen equivalent can be attributed to interstitial solid solution strengthening rather than a variation of the microstructure. It was also found that the final composition of the WAAM samples is mainly controlled by the initial composition of the wire feedstock and not by the interstitial elements pick-up that takes place during manufacturing.

Key words: interstitial elements, Ti-6Al-4V, WAAM, oxygen, directed energy deposition.

7.1 Introduction.

Additive manufacturing (AM) is a novel technology that allows the production of near-net shape parts by the addition of material in a layer-by-layer fashion. Depending on the form of the feedstock AM technologies can be classified as powder or wire-based. The powder-based AM has found great acceptance in the fields where relatively small and complex components are required while wire-based AM has found its application where large scale parts need to be produced. Wire-based methods have received great attention through the Wire and Arc Additive Manufacture (WAAM) technology. In this manufacturing method, an electric arc is used as the heat source, while a metallic wire is fed into the process at a constant rate in order to deposit each of the individual layers. When the system is coupled with a motion system, large and complex geometries can be achieved. Some of the advantages of WAAM as compared to traditional manufacturing methods, such as casting and forging, include significant material savings and shorter lead times due to the design flexibility [1]. Thanks to the capability of using metallic wires as feedstock, the WAAM process can be used to process a wide range of alloys.

Ti-6Al-4V is the aerospace industry workhorse due to its high strength-to-weight ratio and excellent corrosion resistance. Hence, it has been the most investigated titanium alloy system for AM in general and particular WAAM applications.

Despite its outstanding characteristics, titanium has a high affinity for oxygen and it oxidizes when it is exposed to temperatures higher than 480 °C, which represents a concern during AM processes [2]. Oxygen resides in the interstitial lattice vacancies and increases the strength of titanium by solid solution. Similarly, increasing oxygen content can also decrease the ductility levels, it has been established that contents of 0.3 wt% or higher can produce complete brittleness of titanium by restricting slip systems [3]. For this reason, oxygen content control and oxygen pick up during AM have been the focus of various investigations.

The role of oxygen during WAAM deposition of Ti-6AL-4V has been previously reported by Caballero et al [4] and Bermingham et al [5]. The former concentrated on the effect of deposition conditions on alpha case thickness while the latter focused on the sensitivity to oxygen pick up during out of chamber deposition. However, both studies concentrated on the oxygen pick up phenomena during manufacturing rather than the effect of the initial wire interstitial elements on the final mechanical properties of the additively built parts. Similar studies have also been carried out for powder bed fusion of titanium. The main focus has been given to determining the oxygen pick-up levels after powder bed fusion (PBF) processing. Na et al [6] showed that oxygen concentration in the final samples increases linearly as the laser power is increased, oxygen content in the final parts was always higher as compared to the powder feedstock used. In contrast, Park et al [7] found that oxygen content reduced during electron beam melting (EBM). The discrepancy in these finding lies in the fact that the oxygen partial pressures during PBF are high enough to cause oxygen pick up while the vacuum conditions during EBM provides such a low oxygen partial pressure that the thermodynamic requirements for oxygen pick up are not met and oxygen reduction takes place instead. The effect of initial powder characteristics such as particle size distribution, particle morphology, density, and powder flowability on PBF processing and final part quality has also been studied before in several studies [8,9].

In the reviewed literature the effect of initial feedstock composition on final mechanical properties obtained during additive manufacturing of titanium has not been considered before. This work presents a detailed and systematic evaluation of the effect of interstitial contents of the wire feedstock used during WAAM on the tensile properties obtained for Ti-6Al-4V components.

7.2 Materials and methods.

Several Ti-6Al-4V 1.2 mm wires with increasing content of interstitial elements were used for the manufacturing of seven WAAM samples. For each wire, one sample was manufactured. The wires composition as provided by the wire manufacturer are shown in **Table 7-1**.

Table 7-1. Ti-6Al-4V wires composition and oxygen equivalent values.

Wire / wt %	C	O	N	H	Fe	Al	V	Oxygen equivalent (wt %)
Wire 1 (W1)	0.0285	0.185	0.0185	0.001	0.195	6.515	4.005	0.239
Wire 2 (W2)	0.012	0.170	0.016	0.002	0.15	6.01	3.96	0.209
Wire 3 (W3)	0.014	0.170	0.008	0.0029	0.09	5.98	3.95	0.194
Wire 4 (W4)	0.018	0.155	0.0067	0.0009	0.195	6.32	4	0.179

Wire 5 (W5)	0.013	0.150	0.009	0.005	0.131	6.24	4.18	0.176
Wire 6 (W6)	0.006	0.083	0.005	0.0046	0.03	6.02	3.97	0.097
Wire 7 (W7)	0.01	0.058	0.005	0.0058	0.04	5.97	3.97	0.074

The oxygen equivalent value for each of the wires is also shown. The oxygen equivalent was calculated using the formula below. This equation accounts for the combined effect of interstitial elements in terms of solid solution strengthening for titanium [10].

$$[O]_{EQ} = [O] + 2[N] + 2/3[C] \text{ (wt \%)} \quad (7-1)$$

For the WAAM deposition, a 6-axis industrial robot was used in combination with a PTA power source to manufacture the samples. Samples were approximately 320 mm x 130mm x 8 mm and were built on an 11 mm thick Ti-6Al-4V plate. A single pass deposition strategy was used; this consists of single melt beads that are deposited successively one on top of the other until the required height is achieved. A schematic representation of the experimental setup is shown in **Figure 7-1a**. Photographs of a sample built with W4 are shown in **Figure 7-1b**. To minimise oxygen pick up during deposition, the samples were built inside a flexible tent purged with argon. The content of oxygen in the inert atmosphere was in the range of 600-800 ppm. The deposition parameters used are summarised in **Table 7-2**.

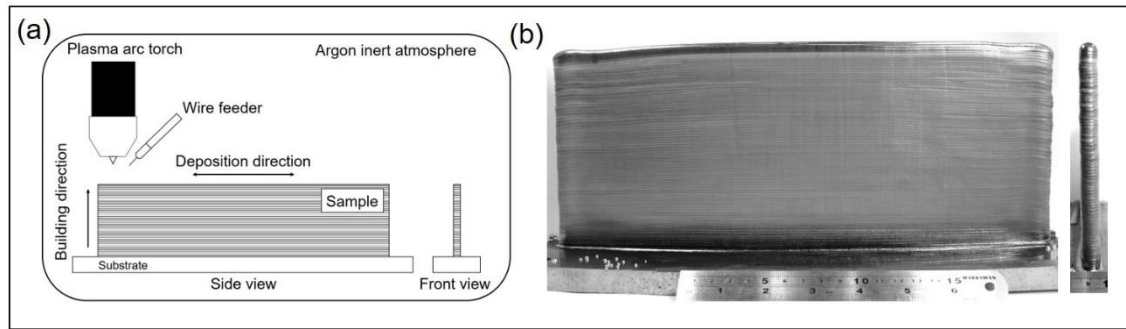


Figure 7-1. (a) Schematics of experimental setup; (b) WAAM sample built with W4.

Table 7-2. Deposition parameters for sample manufacturing.

Current (A)	170
Travel Speed (mm/sec)	5.2
Wire feed speed (m/min)	2.2
Plasma gas flow rate (l/min)	0.8
Shielding gas flow rate (l/min)	15
Torch stand-off distance (mm)	8

After deposition, tensile test coupons were machined out of each sample. Parallel and perpendicular orientations with respect to the deposition direction were tested, these will be referred to hereafter as horizontal (H) and vertical (V) directions respectively. Five samples were tested for each orientation. Tensile coupon extraction locations are shown in **Figure 7-2a**. Samples were tested using the coupon geometry shown in **Figure 7-2b**. The tensile tests were carried out using the guidelines of BS EN 2002-1:2005 standard using an Instron 5500R electromechanical frame equipped with a load cell of 100kN and an extension rate of 0.2 mm/min.

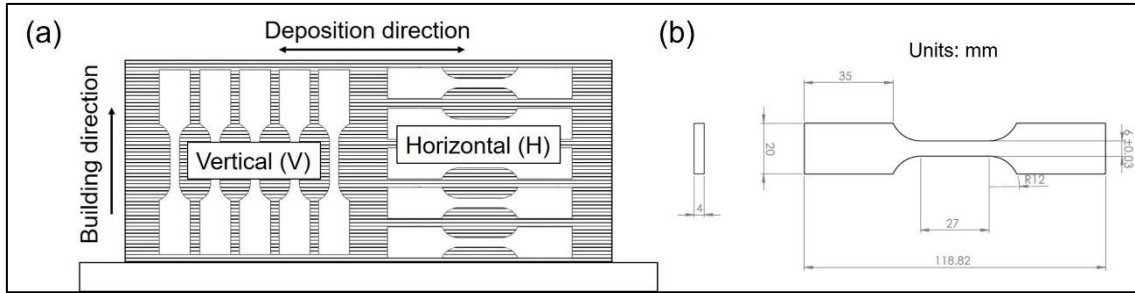


Figure 7-2. (a) tensile coupons extraction locations; (b) Tensile coupon dimensions used for W1, W2, W4 and W7; (c) Tensile coupon dimensions used for W3, W5 and W6.

For the microstructural analysis, samples were prepared using the metallographic procedure reported by Voort [11] and using Kroll's reagent as an etchant. A TESCAN Lyra 3 scanning electron microscope (SEM) in secondary electron mode was used for the microstructural and fractographic imaging. The α -lath thickness average values for samples W1, W4 and W7 were determined following the procedure described by Martina et al [12] and using Adobe Photoshop and ImageJ software for image processing. 15 lines intersect were used per micrograph to measure the α -lath thickness. The reported results were calculated from five micrographs taken from each sample. The micrographs were taken from the middle region between two consecutive generic layer bands. This was done to provide a consistent measurement as it is known that there is a gradient of α -lath thickness between layer bands on WAAM-deposited Ti-6Al-4V [13].

Chemical analysis after WAAM deposition of samples built with W1, W3, W4 and W7 for interstitials content was performed using an inert gas fusion infrared absorption method (LECO). Three samples were measured per specimen and they were extracted from the bulk material at three different locations.

7.3 Results and Discussions.

In **Figure 7-3** and **Figure 7-4**, proof strength (PS) and ultimate tensile strength (UTS) as a function of oxygen equivalent are shown. The values correspond to the average calculated value for both orientations tested, horizontal and vertical. PS and UTS increase linearly as the oxygen equivalent increases. Due to the higher solubility of interstitial elements in the α phase as compared to β , alloys

with higher percentages of α phase experience a significant increase in strength when the content of interstitials is increased [10]. Hence, since Ti-6Al-4V is an $\alpha+\beta$ titanium alloy, the effectiveness of the interstitial elements in increasing strength depends on the volume fraction distribution of the two phases. In the case of WAAM, the as deposited microstructure contains around 90-95 % volume fraction of basketweave α phase (**Figure 7-8**). This is why such a large increase in the tensile strength is observed by increasing the oxygen equivalent from 0.074 wt% to 0.239 wt%. Solid solution strengthening is the mechanism responsible for the increase in the tensile strength of the alpha phase by the addition of interstitial elements [14].

The effect of interstitial elements, other than oxygen, in increasing strength, can be seen from the results obtained for W2 and W3. These two wires have the same content of oxygen in the wire (0.170 wt%). However, higher strength was found for the sample built using W2 as compared to W3 due to its higher oxygen equivalent value. All the wires used in this study comply with the existing quality standard for titanium welding wires, such as AWS A5.16 ER Ti-5 or AMS 4954. However, it has been demonstrated in this work that even slight variations in the chemical composition of the feedstock used for WAAM have an impact on the properties obtained. This shows that specific quality standards have to be developed for additive manufacturing wire feedstock applications in order to have a more consistent and controlled manufacturing process that produces high-quality components.

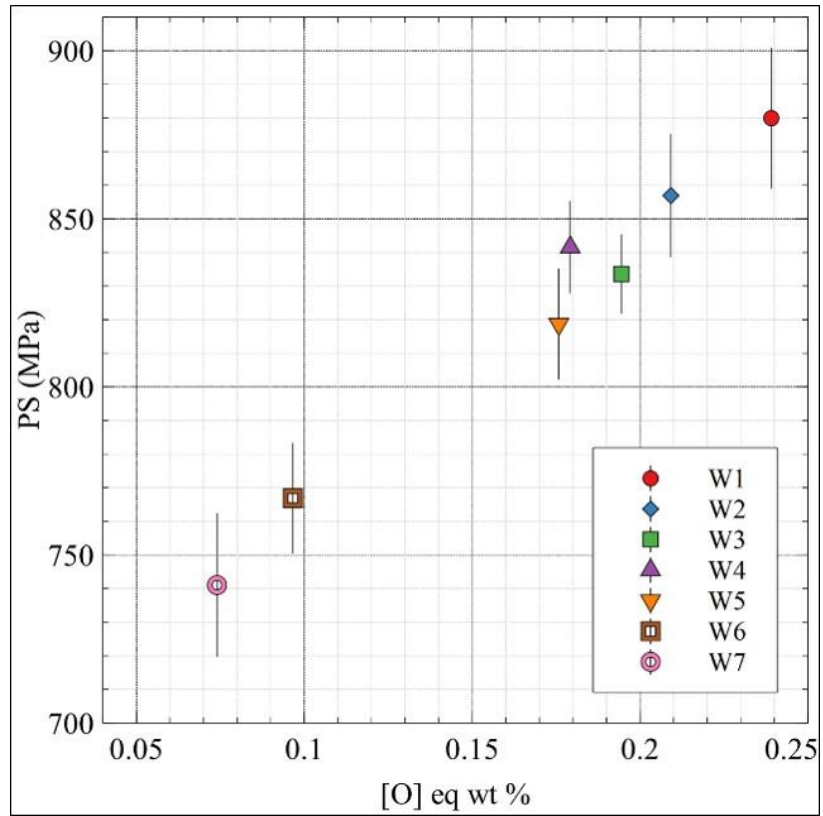


Figure 7-3. Average yield strength as a function of oxygen equivalent. Error bars indicate 95% confidence interval.

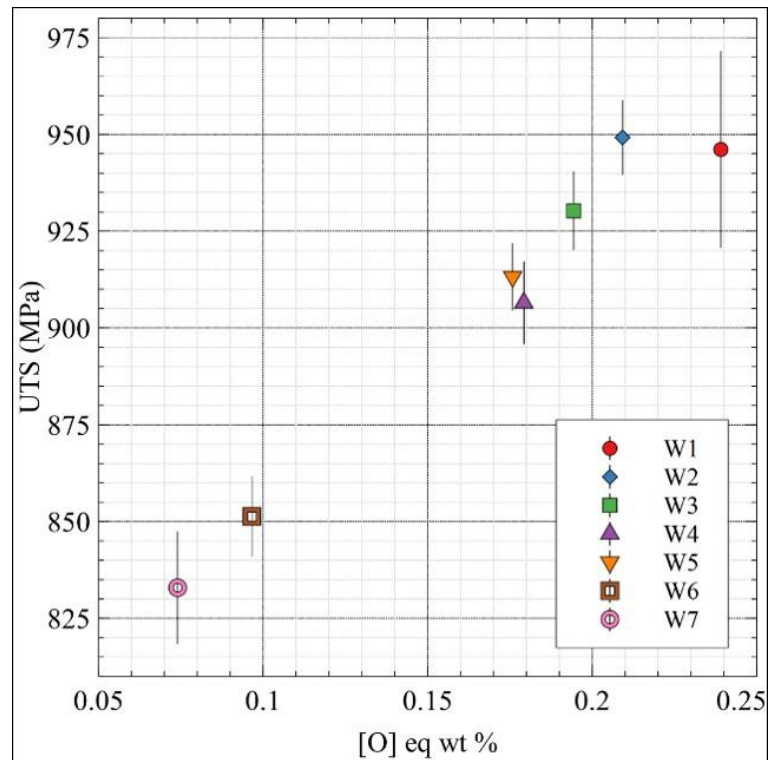


Figure 7-4. Average UTS as a function of oxygen equivalent. Error bars indicate 95% confidence interval.

The effect of oxygen equivalent on elongation is shown in **Figure 7-5**. For the compositional range tested, ductility does not seem to be affected by interstitials content as a variation of oxygen equivalent does not necessarily translate into an increased or decreased elongation. A reason for this is that the embrittlement of Ti-6Al-4V by the addition of interstitial elements is also a function of the microstructure. This means that, depending on the microstructure, the same content of interstitials might have a smaller or bigger effect on ductility. It has been reported before that α' martensitic microstructures are more susceptible to embrittlement by interstitial additions as compared to other microstructure developed in $\alpha+\beta$ titanium alloys, such as bi-modal or lamellar microstructures [15]. Hence, since WAAM deposition produces a dominant basketweave microstructure, an increase of oxygen equivalent of up to 0.239 wt% does not produce severe embrittlement of the deposits. These findings are also in line with previous research that has reported that titanium with a higher intentional incorporation of oxygen, exhibited only a drop from 28% to 26% elongation for increasing oxygen contents of 0.23 wt% and 0.64 wt%, respectively [16]. In this

case, a higher oxygen content was used as an inexpensive way to improve the strength of the components without compromising the ductility and this possibility could be also extended for WAAM of Ti-6Al-4V in future research.

The reason for the higher tolerance of the basketweave microstructure, as compared to a martensitic one, to be embrittled by oxygen additions, has not been clearly reported in the literature and the following mechanisms can be suggested. Ti-6Al-4V relies on both slip and twinning to be plastically deformed and they can be activated individually or simultaneously, and together they determine the ductility of the material [3]. Since Ti-6Al-4V is predominantly an HCP structure at room temperature, the slip systems are limited to only 3 per unit cell which increases the importance of the contribution of twinning for the overall plastic behaviour [17]. However, it has been established that before twinning can take place, oxygen atoms must diffuse away from the octahedral vacancy sites [18]; and since α' martensite in titanium is supersaturated with V atoms, as opposed to the basketweave α -phase [19], these V atoms will generate additional strains into the lattice that will make the diffusion of oxygen more difficult and will retard the occurrence of twinning which results in a decreased ductility. The second mechanism that can be proposed for the lower tolerance of α' martensite to oxygen increments is the fact that the martensitic needles are finer than the lamellar microstructure due to the higher cooling rates used to obtain them. These finer features obstruct deformation by slip and thereby reduce ductility even before the increments of oxygen take place [20].

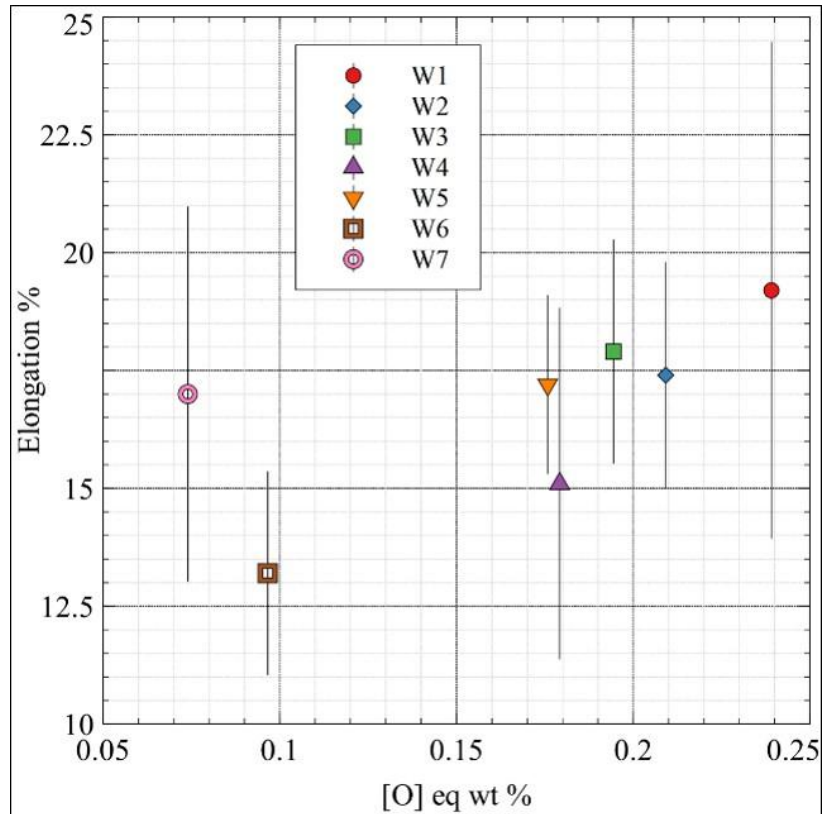


Figure 7-5. Elongation % as a function of oxygen equivalent. Gage length: 20 mm. Error bars indicate 95% confidence interval.

The preservation of good levels of ductility can be further verified by the analysis of the tensile fracture surfaces. Low and high magnification fractographs of the tensile fracture surface are presented in **Figure 7-2a** and **c** and **Figure 7-2b** and **d** for W1 and W6 respectively. Despite having the highest oxygen equivalent, sample W1 is mainly characterized by microvoids coalescence which involves a high degree of plastic deformation, characteristic of a ductile rupture failure mechanism. This supports the fact that increased content of interstitial is not detrimental to ductility. In contrast, W6 shows a mixed-mode of brittle and ductile failure modes which is characterized by a mixture of dimples and flat facets. Showing that, even in the case of lower ductility (W6), a high degree of localized ductility is still preserved.

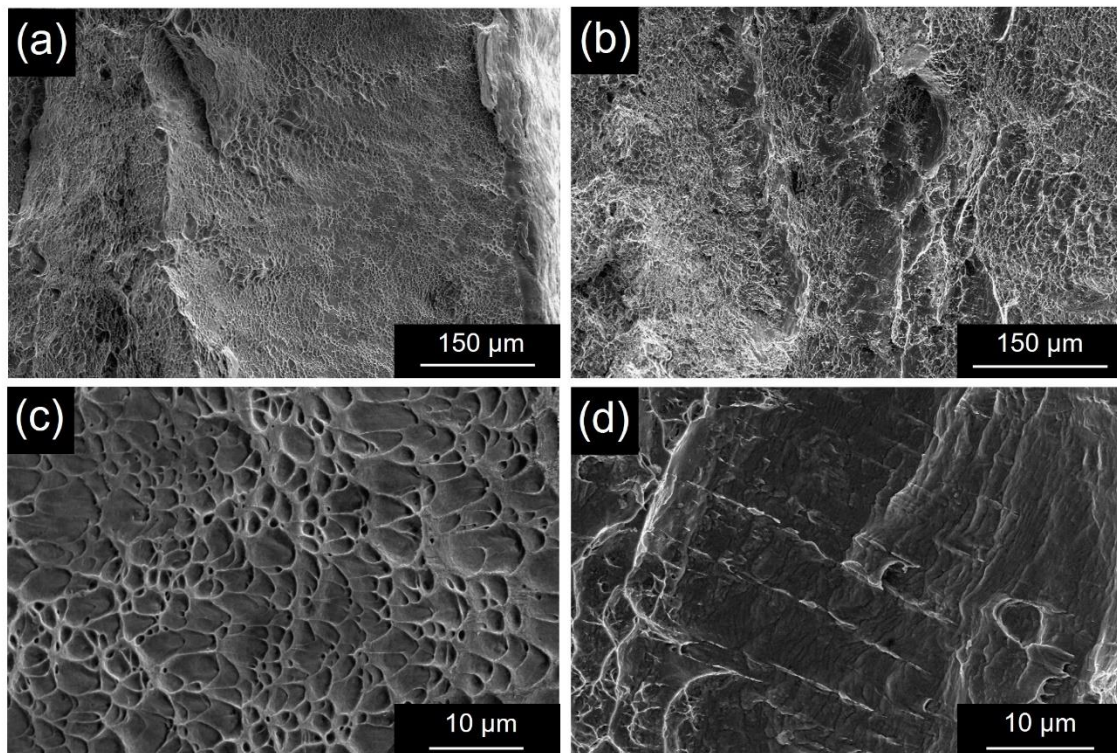


Figure 7-6. SEM images showing the fractography of tensile fracture surfaces of W1: low (a) and high (c) magnifications and W6: low (b) and high (d) magnifications.

Direction specific tensile properties are summarised in **Figure 7-7**. The same trend observed for the average values can be identified. For all the conditions tested, horizontal orientation gives the highest strength and lowest ductility as compared to vertically extracted samples. This behaviour has been seen before for “as deposited” WAAM Ti-6Al-4V and can be attributed to the columnar nature of the prior-beta grains and the strong texture developed during deposition [21].

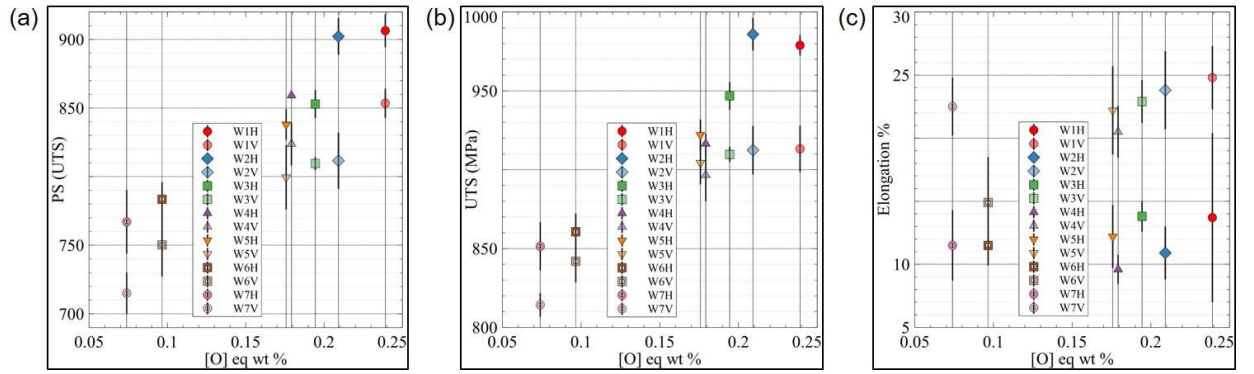


Figure 7-7. Direction specific results for tensile properties. (a) PS; (b) UTS; (c) Elongation %. H: horizontal, V: vertical. Error bars indicate 95% confidence interval.

For $\alpha+\beta$ titanium alloys with a lamellar microstructure, tensile strength is mainly controlled by solid solution strengthening and the α -lath thickness [22]. Hence, the latter aspect was also characterized in the present work. Representative micrographs used to measure the values for the α -lath thickness from sample W1, W4 and W7 can be seen in **Figure 7-8**. Higher strength is usually expected when finer alpha laths are found. Measurements revealed that samples W1 and W4 have an average lath thickness of 1.43 μm and 1.39 μm respectively. While W7 has 1.02 μm . Hence, a higher tensile strength would be expected from this sample. This shows how solid solution strengthening due to interstitial elements plays a more significant role in strength in contrast to microstructural features. Since the deposition parameters were kept constant during the manufacturing of the samples, it can be suggested that the presence of finer α -laths in W7 is a consequence of the difference in chemical composition. According to Rogoff et al [23], the β -transus temperature can be calculated as:

$$\beta_t(^{\circ}\text{F}) = 1545.52^{\circ}\text{F} + 46.26[\text{Al}] + 320.54[\text{O}] + 1375.71[\text{N}] + 894.35[\text{C}] - 17.45[\text{V}] - 57.80[\text{Fe}] \quad (7-2)$$

From this equation, W1 has a β -transus temperature of approximately 1024 $^{\circ}\text{C}$ while W7 has a lower transformation temperature of 973 $^{\circ}\text{C}$. This means that the

$\beta \rightarrow \alpha$ transformation in the latter takes place at a lower temperature which promotes the formation of finer microstructural features.

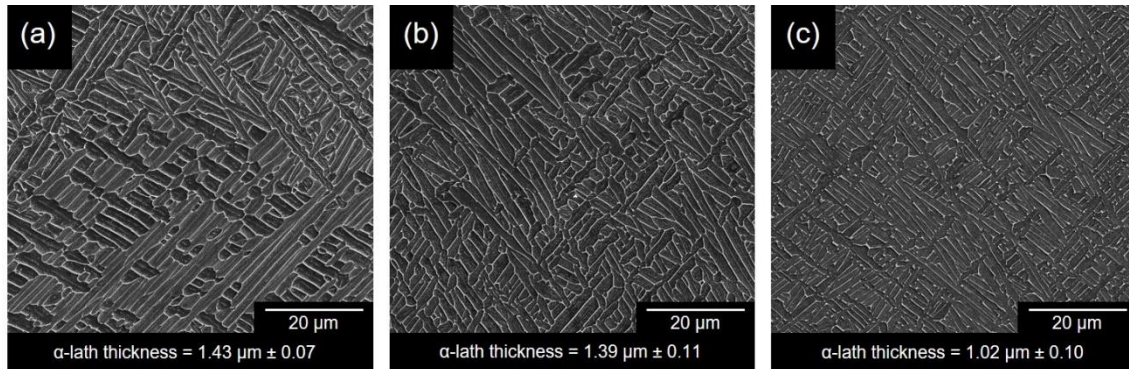


Figure 7-8. Basket weave microstructure of samples built with (a) W1; (b) W4 and (c) W7.

The content of interstitial elements oxygen, nitrogen and hydrogen before (wire) and after WAAM deposition is summarised in **Figure 7-9** for samples W1, W3, W4, and W7. Oxygen pick-up was consistent for all the samples manufactured and it was around 400ppm for all the cases tested. This increase in oxygen content is likely to be caused by the dilution of the oxide scale that exists on the surface of any given layer once a subsequent layer is deposited [4]. Hydrogen and nitrogen showed similar trends. However, for W7, a higher content of hydrogen was measured in the wire before the WAAM deposition, which goes against the trend for the other wires. It can be suggested that this is an experimental error coming from some humidity on the surface of the wire sample before the measurement was taken. This is likely to be the case as the measured hydrogen content for W7, after WAAM deposition, is at the same level as compared to W1, W3 and, W4. As can be seen from these results, the final composition of the components built by WAAM is mainly controlled by the initial composition of the wire rather than the pick-up of interstitial elements during the manufacturing process. Hence, it is verified once again that the initial chemical composition of the wire feedstock is key in the final tensile properties obtained.

Even though the oxygen content of W1 and W3 wires was below the oxygen limit established by the relevant quality standards of 0.2 wt%, it is clear how, after WAAM deposition, this value increased past this threshold. However, as the

tensile data presented in this work demonstrated, strength was improved without compromising the elongation when higher content of oxygen exists. This helps to further support the aforementioned explanation that the $\alpha+\beta$ basketweave microstructure formed during WAAM of Ti-6Al-4V is much less susceptible to embrittlement by oxygen addition as compared to other microstructures such as martensite. This could be considered as an advantage of WAAM as compared to other AM technologies such as PBF. During PBF, faster cooling rates are experienced as a consequence of the high-power density of the energy source. This generally creates a predominant α' martensitic microstructure that has been shown to exhibit signs of severe embrittlement at levels of oxygen as low as 0.15 wt% [24,25]. In contrast, it has been reported in the literature that components with lamellar $\alpha + \beta$ microstructures with oxygen contents up to 0.36 wt% can preserve good levels of ductility [15,26]. Hence, it can be suggested that Ti-6Al-4V components manufactured by WAAM should exhibit a similar tolerance to increased levels of oxygen.

Oxygen pickup during WAAM was also characterized by Bermingham et al [5]. In this work, a sample was manufactured with no additional shielding method apart from the shielding gas provided by the torch. LECO measurements after deposition revealed a pickup of oxygen of only 300 ppm even though visual inspection revealed apparent severe oxygen pick up on the surface of the sample. Additionally, elongation did not decrease significantly as compared to the control condition where the sample was built in optimum shielding conditions using a local trail shielding device. The authors argued that the reason for this is that oxygen pick up takes place once the molten metal has solidified and the effect of oxygen diffusion is limited. These results, together with the results reported in the present work can be used to propose that the risk of compromising the mechanical properties by increasing the content of oxygen during WAAM deposition is very low, even if the shielding conditions are poor. Moreover, even if oxygen contamination does take place, the developed microstructure during WAAM of Ti-6Al-4V has a very low susceptibility to losing ductility as a consequence of the incorporation of oxygen.

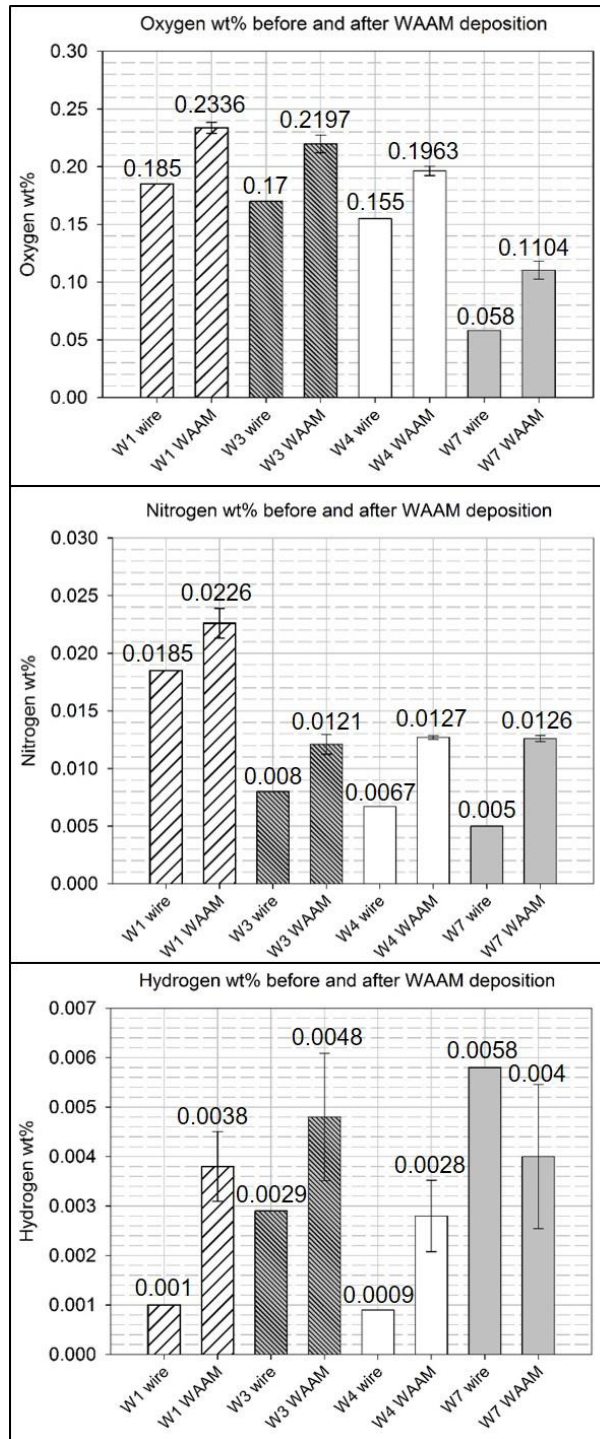


Figure 7-9. Interstitial content before and after deposition for samples built with W1, W3, W4 and W7 wires.

7.4 Conclusions.

This study investigated the effects of initial wire feedstock composition on the final tensile properties of Ti-6Al-4V produced by WAAM. Seven samples were produced using seven different wires with increasing content of interstitial elements. The main findings can be summarized as follows:

- Proof strength and ultimate tensile strength increase linearly with increasing oxygen equivalent content. An increase of at least 100 MPa was found between the lower and highest interstitials content tested.
- Wire feedstock composition that complies with current welding wire quality standards can produce a wide range of tensile properties values after WAAM deposition, depending on slight variations in the chemical composition. This proves that more specific quality standards have to be developed for WAAM feedstock.
- For the oxygen equivalent range tested, ductility is not compromised by increasing the content of interstitial elements.
- Lamellar $\alpha+\beta$ microstructure formed during WAAM of Ti-6Al-4V proved to have small susceptibility to embrittlement due to the addition of interstitial elements within the tested range as compared to other microstructures such as α' martensite.
- Solid solution strengthening by interstitial elements plays a major role in determining mechanical strength as compared to microstructural features.
- The final content of interstitial elements of additively built components by WAAM is mainly controlled by the initial composition of the wire feedstock rather than the pick-up of interstitial elements during manufacturing.

7.5 References.

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8 Summary.

8.1 Overall discussion.

This thesis focuses on evaluating the criticality of various processing conditions on the performance and mechanical properties of various processes and materials manufactured by AM. The implications of the findings of this work within the context of the field of additive manufacturing are summarised below:

8.1.1 Effect of shielding conditions on melting stability and mechanical properties of AM components.

The findings for the effect of shielding gas composition on the melting stability of SS304L during L-PBF indicated that shielding gas ionisation potential is critical to ensure a stable melting process suitable to generate defect-free components with no discontinuities such as pores or cracks. For example, helium was shown to improve and stabilise the melting behaviour during laser-powder interaction as compared to argon. Usually, it is assumed that fibre lasers, the main laser source type used to manufacture commercial L-PBF machines, are not susceptible to varying shielding gas composition thanks to their wavelength. However, it was proved in this work that this is clearly not the case due to the small laser spot size needed for the L-PBF process. This assumption has led to the fact that argon is used as the conventional shielding atmosphere in most industrial practices. To some extent, this approach seems to work well because the normal procedure to find “optimal” process parameters is to develop a parametric experimental matrix to test hundreds of process parameters combination such as laser power, travel speed, and hatch distance until suitable conditions are found based on which combination can provide the densest parts. The reason for these parameters working, even under an argon atmosphere, can be attributed to the fact that certain combinations can allow the remelting of previously consolidated layers that can help to minimise defects generated in previous layers as a consequence of an unstable melting regime obtained by using argon. However, this means that the potential of stabilising the melting process to increase the robustness of the process by using helium remains largely unexploited and required further investigation and implementation.

In terms of the relationship between shielding gas composition and microstructure developed for the additive manufacturing of 17-4PH, the experimental results obtained in this work showed that the microstructure of this alloy is not strongly dependent on the shielding gas composition for WAAM deposition, particularly in the percentages of retained austenite obtained. This phase is normally undesirable on these alloys as it can generate inconsistent strain behaviour due to stress-induced transformation and because it cannot be age hardened. This contrasts with the manufacturing of 17-4PH components by L-PBF where the shielding gas used during the manufacturing of the powder can greatly increase the volume fraction of retained austenite by altering the composition making it impossible to achieve the properties of the wrought counterpart even after post-deposition heat treatments . This is due to the fact that in L-PBF of 17-4PH, nitrogen (an austenitic phase stabiliser) is normally used as shielding gas whereas in arc-based AM only mixes of argon, carbon dioxide and helium are used . It is also noteworthy to mention that it was possible to identify, from the revised literature, that even the gas used during the atomisation process of the 17-4PH powder can determine how much retained austenite is obtain in the final additively built product. However, this is not a problem for the WAAM deposition of 17-4PH as the feedstock used is a wire that has a very similar composition to the wrought material that has been drawn from a billet.

8.1.2 Effect of different thermal conditions on the final microstructure and mechanical properties of 17-4PH and Ti-5553.

This work explored how different thermal cycles can affect the microstructure and mechanical properties of two age-hardenable alloys, 17-4 PH and Ti-5553. Different thermal histories were achieved by either changing the deposition strategy used, which will determine how the heat is applied to the part and how it will distribute, and by using different interpass temperatures during WAAM. Ti-5553 showed high sensitivity to different thermal cycles as the α phase nucleation and growth are closely related to the characteristic of each heating and cooling cycle of the deposition process. On the other hand, 17-4 PH showed some scatter on the hardness measurements by using different deposition strategies, but no significant differences were observed, suggesting minor changes in the

microstructure. Since 17-4 PH is an age hardenable alloy, hardness is a representative measure to indicate the state of the precipitates and thus the mechanical properties. These results show the importance of alloy selection for AM processes. Some alloys are more susceptible to the cyclic heating cycles of additive manufacturing while others can have better tolerance in modifying their mechanical properties due to the inherent microstructural heterogeneities. Hence, factors such as the sensibility of the material for microstructural changes under different thermal cycles should be part of the alloy selection criteria when choosing a specific alloy to be used for an additive process.

8.1.3 Effectivity of post-deposition heat treatments on the final microstructure and mechanical properties of 17-4PH and Ti-5553.

Post-deposition heat treatments were applied to the age-hardenable alloys studied in this work to optimise mechanical properties. For 17-4PH, the standardised heat treatment proved to be successful in producing mechanical properties as good as the wrought components, independent from the shielding gas and thermal cycles used during manufacturing. No modifications on dwelling temperatures or aging times had to be made. It is likely that the positive effect of the heat treatment does not depend on the starting grain morphology (columnar or equiaxed) as it was shown on this work that the effectivity of the heat treatment relies on the braking down of the dendritic microstructure and further aging that would be very similar regardless of the initial grain's morphology. These observations, together with the fact that WAAM does not retain a high-volume fraction of retained austenite for 17-4 PH, means that WAAM is a more suitable process than L-PBF for the manufacturing of 17-4 PH. Therefore, it should be selected when possible, to ensure the highest quality and mechanical performance of components additively made out of this alloy.

For Ti-5553, the scenario is a bit different. Initially, the results showed that good levels of strength and elongation can be obtained in the as-deposited condition directly after conventional WAAM deposition using a plasma transfer arc as the power source. The mechanical properties were even higher than the ones reported in the literature for powder-based processes in the same condition. The

reason for this is that the thermal cycles inherent to WAAM provide the right conditions of temperature and time to nucleate and grow the α phase lamellar microstructure which is the phase responsible for the mechanical performance of Ti-5553. Nevertheless, even though the strength was satisfactory, elongation showed high anisotropy which is attributed to the large and coarse β -grain structure. Hence, conventional plasma WAAM deposition process was modified to obtain a more refined and equiaxed microstructure. This was achieved successfully by increasing the wire feed speed by adding an extra feeding wire. However, this created new challenges as it was identified that a higher fraction of grain boundaries, which is a direct consequence of having smaller equiaxed grains compared to large and columnar ones, promoted the formation of grain boundary α -phase which significantly decreased the plastic performance of the material. For this reason, the standard heat treatment applied for Ti-5553 has limited effectivity and it is not possible to obtain a good strength performance while preserving acceptable levels of ductility. This is normally not an issue for traditional forging of Ti-5553 which can be attributed to the fact the forged bimodal microstructure, differs from the fully lamellar structure that is invariably obtained after WAAM deposition on its strain response to applied stress. It is expected that if the starting microstructure of Ti-5553 is formed only by large columnar β -grains then the fraction of grain boundaries is significantly reduced and the formation of the detrimental $GB\alpha$ would be limited, increasing the chances of applying an effective heat treatment successfully at the expenses of a potential anisotropy that could still exist due to the parent columnar structure. Therefore, a key challenge to extend the application of Ti-5553 for WAAM was identified in this work and these findings serve as a good starting point to further optimise the processing of Ti-5553.

In terms of applying the heat treatment to large parts of complex geometry with considerable wall thickness, then the effectivity of these aging heat treatments would have to be reassess. It is known through the concept of hardenability that there is only a maximum strength than can be achieve for a particular alloy related to the maximum cooling rates that can be achieved at the core of the material due to large thermal masses, and AM built components would be of no difference

in that sense. However, due to the layer-by-layer nature of the additive process this challenge could be overcome by dynamically controlling the heating and cooling rates during deposition to produce and in-situ heat treatment. Alternatively, thanks to the process design flexibility of AM, smaller sections of a much larger thicker component can be built in steps and the heat treatment can be applied on each of the successive steps with the aim of obtaining a properly heat-treated component as final product.

8.1.4 Role of interstitial elements on the WAAM of Ti-6Al-4V.

One of the main concerns for the additive manufacturing of titanium alloys, and particularly Ti-6Al-4V is interstitial element pick up, particularly oxygen, which can occur during the WAAM deposition causing severe embrittlement of the material. Currently, there are no clear limits established on how much oxygen can be allowed. By systematically studying how the increment of interstitial content on the WAAM wire feedstock affected the mechanical properties, it was possible to establish a better understanding of what these limits are. For example, one of the commonly used standards for titanium bars and forgings for aerospace applications specifies that the oxygen content cannot be higher than 0.2wt% (AMS 4928). However, from the data collected in this work, it was identified that the ductility of the material was not compromised even for excess oxygen contents of 0.23wt%. Furthermore, the increasing oxygen content did not cause any sudden drop of ductility and whilst providing a linear increase of the tensile strength. This higher compatibility of oxygen and other interstitial element incorporation is attributed to the fact that the fully lamellar microstructure developed during WAAM deposition has a good tolerance, better than usually thought, before it is severely embrittled by oxygen. This is not the case, for instance, for Ti-6Al-4V components made by L-PBF as it has been reported in the literature that this microstructure is mainly martensitic which has been shown to be severely embrittled by much lower oxygen content increments. Hence, it is clear that work has to be done on creating new specific quality standards that consider the variables of each specific additive process and that can provide updated compositional ranges that actually identified the limits for interstitial

elements are before the mechanical properties are compromised. This is of utmost importance because if accurate limits for oxygen content for Ti-6Al-4V are clearly identified, then oxygen could be used as an inexpensive way to improve the strength of WAAM components, especially in the cases when coarse α laths of lower strength are obtained due to large heat build-up. Similar to how it is currently done for commercially pure titanium. In addition to this, clearly identifying the limits for oxygen concentration can help increase the flexibility in the shielding atmosphere which can lead to cost reductions and easier automation of the process.

8.2 Contribution to knowledge.

This work has identified critical various processing conditions for a range of additive manufacturing processes and materials. The following intellectual contributions have been made to the field of additive manufacturing:

1. The shielding gas composition (gas ionisation potential) on laser powder bed fusion (L-PBF) additive manufacturing processes is critical to ensure melting stability. A stable melting regime and a consistent bead geometry can be achieved by using the right shielding conditions.
2. Different shielding conditions and deposition strategies do not have a significant effect on the microstructure and mechanical properties of WAAM deposited 17-4PH. The final properties are controlled by the post-deposition heat treatment applied and not by the deposition parameters used.
3. The microstructure developed during WAAM deposition of Ti-5553 is highly dependent on the thermal conditions applied. However, in-situ aging takes place during WAAM deposition of Ti-5553 that resembles its wrought counterpart which, producing high values of tensile strength in the “as-deposited” state when the β -grain structure.
4. A refined β -grain structure for WAMM deposited Ti-5553 is susceptible to severe embrittlement due to the presence of grain boundary α phase. This phase must be kept to a minimum to avoid this issue.

5. Systematic investigation regarding the effect of interstitial elements on the tensile properties of WAAM deposited Ti-6Al-4V, revealed that the microstructural features developed during deposition of Ti-64 are not susceptible to embrittlement due to an increased content of interstitial elements under the standard operating condition of the WAAM process. Even when the values are higher than the maximum concentrations established by the current quality standards.

8.3 Future work.

The work completed as part of this thesis can be extended into the following research directions:

8.3.1 Optimisation of shielding gas composition.

It was determined in this work that the presence of helium in the shielding gas can significantly improve the melting stability during laser-powder interaction making it possible to better control the bead shape obtained that can potentially minimise defects. However, only an atmosphere of 100% helium was investigated which could represent practical complications in terms of cost and technological challenges. Hence, to fully take advantage of the benefits of adding helium, more research needs to be conducted using different contents of helium to achieve various ratios of the argon-helium mix. The aim would be to determine if the benefits of helium can be observed by using it at smaller percentages. If the same kind of melting stability can be reproduced by using an optimal helium content, then the adoption of this practice could be easily extended to real manufacturing processes. Additionally, it would be useful to investigate if the same stabilising effect on the melting occurs for other alloys. Metal vapours, that come from the material being melted, form part of the plasma plume and they can change its composition and ionisation behaviour. For this reason, it would be beneficial to verify that the stability of using helium can be extended to the wide range of alloys used in laser powder fusion processes.

8.3.2 Mechanical properties optimisation of WAAM deposited Ti-5553.

Further investigations are required to improve the mechanical properties of Ti-5553, in particular the plastic behaviour. The post-deposition heat treatment apply to the WAAM material with a refined β -grain structure needs more investigation as the standardised heat treatments are not likely to produce successful properties. A heat treatment needs to be developed aimed at minimising the grain boundary α . Two routes can be recommended as the starting point in this work. One option could be to ensure rapid cooling rates after the solution treatment has been applied, preferably cooling rates faster than $1^{\circ}\text{C}/\text{sec}$ would be best as the CCT diagram shows that cooling rates faster than that do not produce any further α precipitation. The soaking times and temperature for the solution stage need also to be investigated as it is necessary to dissolve as much as possible the grain boundaries α formed during the deposition process without generating excessive grain growth. Another alternative for heat treatment would be to produce a microstructure formed by coarse and much finer α laths. This mixture of coarse and fine features could improve the ductility by better distributing the strain applied while still providing acceptable levels of strength thanks to the fine laths. Such morphology could be obtained by solutionizing the material followed by holding it at a sub-transus temperature ($700\text{-}800^{\circ}\text{C}$), then cooling down to room temperature, and then aging as normal. Processes with a lower heat input can also be investigated for the WAAM deposition of Ti-5553. Since the formation of grain boundary α and precipitation-free zones are a diffusion process, keeping the material at a lower temperature and minimising the dwelling times at high temperatures during a deposition could reduce the precipitation of these detrimental phases in the first place.

8.3.3 Identification of oxygen concentration limits of WAAM deposited Ti-6Al-4V.

Even though this work identified that the microstructure developed during WAAM deposition of Ti-6Al-4V has a good tolerance to oxygen, the upper limit that this alloy can handle before the ductility starts to significantly decrease is not yet identified. Hence, additional trials are required to determine accurately what

these limits are. This can be done by using wire feedstock with even higher starting levels of oxygen content than the ones used in this work, or it can also be investigated by adding oxygen during the deposition process itself by carefully controlling the amount of oxygen in the plasma torch shielding. Once the oxygen limit is identified by measuring the ductility, then further mechanical testing, especially fatigue, and damage tolerance need be performed in order to issue the final oxygen acceptance level for WAAM-built Ti-6Al-4V components.

The data collected on this work was obtained from only one type of shielding approach, known as global shielding. Hence, it would be advantageous to explore other shielding options, such for example local shielding (an approach similar to trail shielding for welding) in order to identify if similar pick-up levels of oxygen could be achieved that would not compromise the ductility. It could also be explored if the shielding provided from the PTA torch can be enough to provide suitable shielding conditions were the deposition parameters can provide small enough melt pools that would be shielded by the torch during the whole duration of solidification, where the material is far more susceptible to oxygen embrittlement as compared to the solid state.

