



**Improving ductility and fracture toughness of as-built Ti-6Al-4V parts
fabricated using powder bed fusion processes by in situ alloying**

MSc RESEARCH DISSERTATION

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Abstract

Ti-6Al-4V is a titanium alpha-beta ($\alpha+\beta$) alloy used in the aerospace industry. The CSIR-National Laser Centre encountered problems building large Ti-6Al-4V parts by additive manufacturing using the AeroswiftTM machine. The acicular α' microstructure of Ti-6Al-4V had low fracture toughness and ductility, resulting in the part being unable to withstand the residual stresses, and delaminating during processing.

To solve this problem, *in situ* alloying of Ti-6Al-4V with a ductile beta (β) stabilizer, 10 wt% Mo, was investigated since the β phase is more ductile. Samples were manufactured on the powder bed fusion (PBF) and directed energy deposition (DED) platforms. A commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) was also investigated for comparison.

The Ti-6Al-4V, Ti-6Al-4V+10 wt% Mo and β -Ti alloy samples were manufactured on a selective laser melting (SLM) machine (PBF process), and Ti-6Al-4V+10 wt% Mo samples were made on a LENSTM machine (DED process). The samples were subsequently examined by optical, scanning electron microscopy (SEM) with electron diffraction X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD), X-ray diffraction (XRD), and were tested for hardness.

Increased energy density changed the shape of pores, and decreased the porosity. The microstructure of PBF-produced Ti-6Al-4V+10 wt% Mo was inhomogeneous, with unmelted Mo particles and inconsistent hardness values, depending on Mo content. A PBF sample was tested for micro-galvanic corrosion, and the more Mo particles were attacked. Thus, no further testing was conducted on this alloy. The overall alloy hardness (302 HV_{0.3}) was lower than for Ti-6Al-4V (360 HV_{0.3}), indicating that Mo had a softening effect. When produced by DED, Ti-6Al-4V+10 wt% Mo was more homogeneous, with very little unmelted Mo, and hardness was higher (397 HV_{0.3}) than for the PBF sample (302 HV_{0.3}). The commercial β -Ti alloy had a fully β microstructure, with a 309 HV_{0.3} hardness, which was lower than that of Ti-6Al-4V (360 HV_{0.3}). The ultimate tensile strength of Ti-6Al-4V (1130 MPa) was higher than for the commercial β -Ti alloy (863 MPa). The elongation of the commercial β -Ti alloy (30%) was much higher than Ti-6Al-4V (9%).

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List of contributions

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2. Madikizela, C., Cornish, L.A., Chown, L.H., Arthur, N. and Moller, H. (2017). Comparison of *in situ* alloyed Ti-6Al-4V+10Mo via selective laser melting and laser metal deposition, *18th Annual International RAPDASA Conference*, Durban, South Africa, 8-10 November 2017.

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List of Abbreviations

2D	Two dimensions
BCC	Body Centred Cubic
CAD	Computer-Aided Drawing
CSIR	Council for Scientific and Industrial Research, Pretoria
DED	Directed Energy Deposition
EBSD	Electron backscatter diffraction
EDX	Electron Diffraction X-ray Spectroscopy
EOS	Electro Optical Systems
HCP	Hexagonal Close Packed
HV	Vickers hardness
LENS	Laser Engineering Net Shaping
PBF	Powder Bed Fusion
SEM	Scanning Electron Microscope
SLM	Selective Laser Melting
UTS	Ultimate Tensile Strength

Chapter 1: Introduction

1.1 Background

Since their invention in the 1960s, lasers have been a technology surrounded by interest and have received extensive research. As more and more uses were discovered, their potential to pioneer the manufacturing industry in the future also increased. A future where there is less waste and material loss and higher production efficiency with infinite geometries and shapes is now possible.

Lasers coupled with titanium with its impressive mechanical properties are of interest in research due to their potential to improve the manufacturing industry. The laser processing of titanium and its alloys will ensure that parts with good mechanical properties are built efficiently, at lower production times, saving money as opposed to current practices using conventional methods. Laser-based additive manufacturing is a process where a laser is used to manufacture a part layer by layer using a CAD model (Kumar and Pityana, 2010). The current research is focused on the growing interest to produce parts for the aerospace industry using laser-based processes such as powder bed fusion, or PBF (Herderick, 2011). In January 2016, the largest commercially available machine had a build envelope of 800 x 400 x 500 mm³, compared to the previously available build envelope of 250 x 250 x 250 mm³ (Concept Laser, 2016; EOS, 2016). Due to this improvement, larger parts can be manufactured, making this process more suitable to a wider range of applications. Some processing disadvantages arising from laser-based additive manufacturing are anisotropy, porosity, poor surface quality, internal residual stresses and a lower ductility than achieved by conventional methods such as casting (Thijs *et al.*, 2010).

In order for laser-based additive manufacturing to replace conventional manufacturing techniques, it must produce matching or superior mechanical properties. Figure 1.1 (Vrancken *et al.*, 2012) compares the stress-strain curves of wrought and selective laser melted (SLM) titanium alloy Ti-6Al-4V. The SLM process produces parts with higher strength, but inferior ductility and fracture toughness (the area under the curves in Figure 1.1). This implies the part is unable to resist the high residual stresses during processing, causing it to crack and warp. Consequently, this makes unmodified Ti-6Al-4V an unsuitable alloy for high power PBF processing. This project concentrated on the poor ductility (<10% elongation) and low

fracture toughness of Ti-6Al-4V resulting from formation of the acicular Ti-rich martensitic α' microstructure and internal residual stresses which led to cracking and delamination of these parts. Beta titanium alloys are known for their high ductility and fracture toughness compared to $\alpha+\beta$ alloys. This work investigated increasing the fracture toughness and ductility in two ways. Firstly, by modifying Ti-6Al-4V by alloying it with a beta (β) stabilizing element, molybdenum, to make a fully β -Ti alloy *in situ*, which is expected to increase ductility and other mechanical properties, such as fatigue resistance and fracture toughness by stabilizing the β phase (Vrancken *et al.*, 2014). Secondly, by investigating the use of a commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo), which has a high ductility (13% elongation) (Matweb, 2017). This β -Ti alloy was chosen because of its ductility value and its availability at the start of this project. To cover the full implications of alloying *in situ*, the Ti-6Al-4V+10 wt% Mo alloy was also processed by directed energy deposition (DED) in order to compare the effect on the microstructure and mechanical properties.

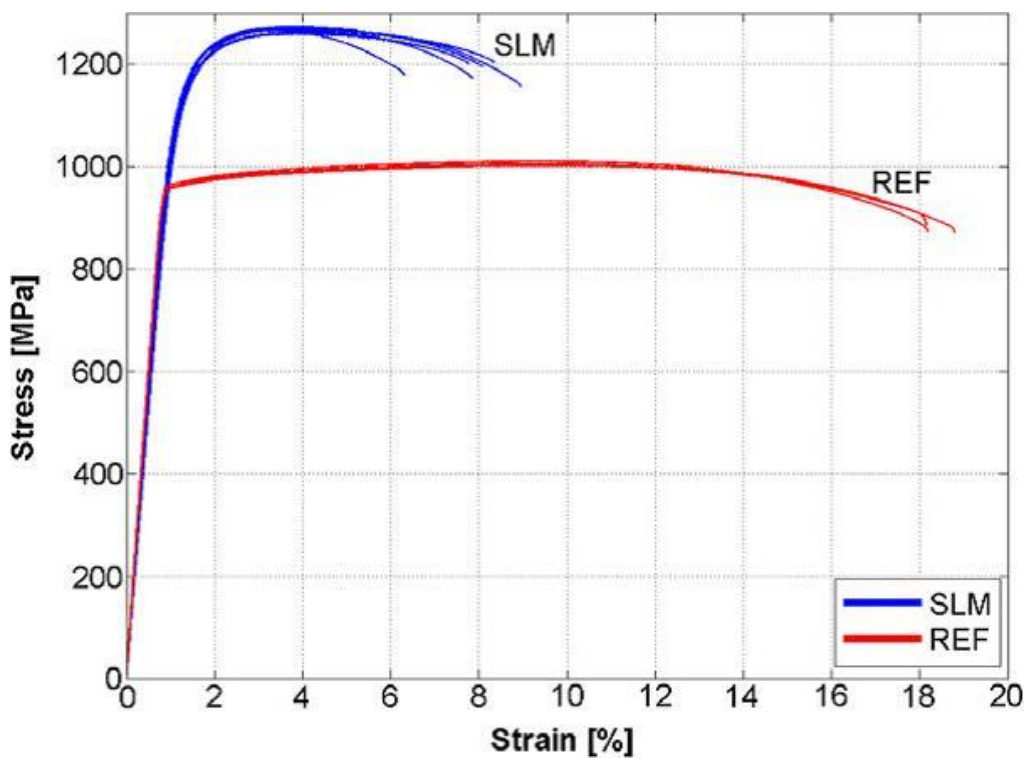


Figure 1.1: Stress-strain curves for SLM produced Ti-6Al-4V and wrought Ti-6Al-4V (Vrancken *et al.*, 2012).

1.2 Gaps in existing body of knowledge and significance of the current research

Fischer *et al.* (2016) recognised the scarcity of obtaining commercial titanium alloys in powder form. These alloys are available as pre-alloyed material which has to be gas atomised to obtain powder. Elemental powder is more readily available; therefore, if these alloys could be manufactured *in situ*, it would be beneficial, especially in the development of new alloys. It was therefore worthwhile to investigate whether *in situ* alloying would be a viable alloying option for PBF processing, which is a fairly new process that needs a more suitable material (more ductile) than Ti-6Al-4V for larger parts. Fischer *et al.* (2016) also concluded that *in situ* alloying made it possible to adjust the compositions of alloys and this could potentially be used to manufacture alloys which are not commercially available as powders. Vrancken *et al.* (2014) investigated adding 10 wt% Mo to Ti-6Al-4V using PBF processing, finding that 10 wt% was sufficient to fully stabilize the β -Ti phase and therefore improve fracture toughness and ductility. At the time of initiating the project, no work had been done on adding 10 wt% molybdenum (Mo) to Ti-6Al-4V for high power, high speed PBF processing to achieve the same improvement in properties, therefore this was covered in the current project.

At the time of writing, work done on laser-based additive manufacturing had not reported the use of a high power laser of 5 kW (Vrancken *et al.*, 2014; Xu *et al.*, 2015). The higher power, aided by controlling parameters such as hatch spacing and laser spot size, would allow for higher power densities (Kannatey-Asibu, 2009). A high power density would make higher processing speeds achievable. This project added to the current knowledge base in additive manufacturing, by attempting to create large parts faster and more efficiently with superior properties than conventional methods achieved using low power lasers. AeroswiftTM has a build envelope of 2000 x 600 x 600 mm³, and plans to build parts this large, so this size is the target for “large parts”.

Work has been done by Vrancken *et al.* (2014) on Ti-6Al-4V alloyed *in situ* with Mo by PBF processing and Collins *et al.* (2003) worked on commercially pure titanium alloyed *in situ* with Mo by DED processing. However, work was done for the first time in this project on Ti-6Al-4V alloyed *in situ* with Mo by DED processing. The DED process is not used for building large parts at higher speeds therefore it was only used for comparative purposes.

1.3 Problem statement

Laser-based additive manufacturing is a growing industry. The Ti-6Al-4V alloy is one of the preferred alloys used in the aerospace industry (superior mechanical properties), hence the focus on this material for this research. The aerospace industry is interested to manufacture parts using a PBF process. This process deposits powder by coating it onto a base plate using a scraper, prior to melting the powder with a laser (Kumar and Pityana, 2010). However, the major problem is that due to the acicular α' microstructure which causes poor ductility, the parts tend to crack. PBF processes are preferred, because of their rapid production times, dimensional accuracy, improved strength compared to conventional methods and reduced material wastage (Xu *et al.*, 2015). Figure 1.2 shows a part that was produced using a PBF process. As the part could not withstand the internal stresses, it delaminated from the base and deformed to such an extent that manufacturing had to be stopped. Increasing the ductility and fracture toughness of the metal would decrease the probability of cracking during processing, and would make PBF more competitive than parts produced by conventional methods in terms of mechanical properties. The main aim of this work is to investigate whether modifying Ti-6Al-4V *in situ* to make a β -Ti alloy was more beneficial than finding a suitable commercial β -Ti alloy which already had a high ductility and fracture toughness.

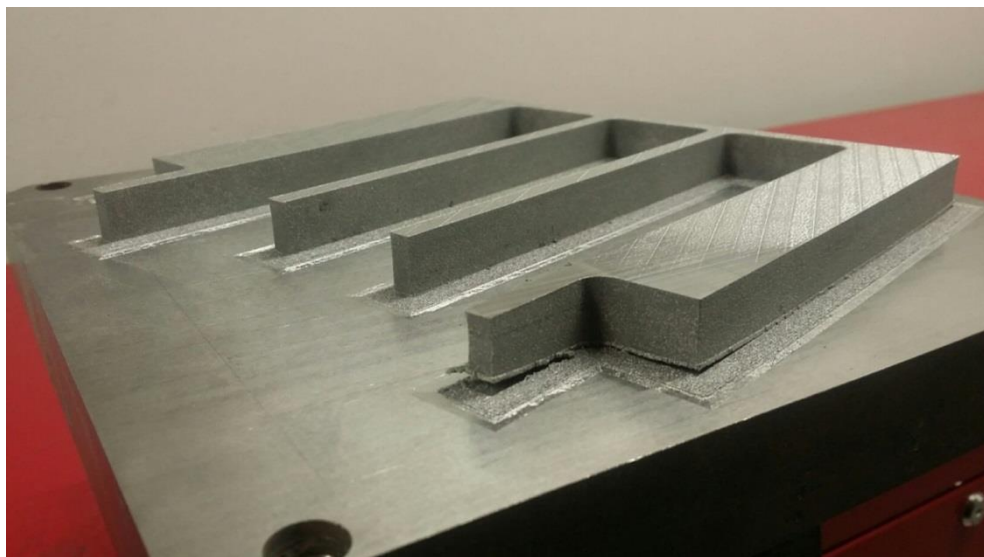


Figure 1.2: Delamination and cracking of Ti-6Al-4V part produced by a PBF process (Produced at the CSIR-NLC, 2015).

This research aimed to answer the following questions:

- Would the addition of 10 wt% Mo to Ti-6Al-4V fully stabilize the β -Ti phase when high power and high speeds are used?
- Would the microstructure of Ti-6Al-4V alloyed *in situ* with 10 wt% Mo be suitable for the aerospace industry?
- Would the PBF process or DED process produce a homogeneous microstructure of Ti-6Al-4V+10 wt% Mo alloyed *in situ*?
- How would the microstructures formed in these two processes (PBF and DED) affect the micro-Vickers hardness?
- How would the microstructure and mechanical properties of Ti-6Al-4V compare to those obtained from a more ductile commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo)?
- Would the β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) have the potential to be used instead of Ti-6Al-4V in the manufacturing of large parts?

1.4 Research objectives

The research objectives were:

1. To identify processing parameters that would give good build qualities for the Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo alloy.
2. To produce samples of Ti-6Al-4V+10 wt% Mo alloy using the PBF and DED processes.
3. To characterize and compare the microstructure and Vickers hardness of the samples produced and deduce which process is the most suitable for *in situ* alloying.
4. To produce samples using a commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo).
5. To characterise and compare the microstructure and mechanical properties of the β -Ti alloy, Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo samples.

1.5 Delineation and Limitations

This project only investigated the as-built condition of the samples and the only mechanical properties considered were hardness, ultimate tensile strength, 0.2% yield strength and fracture toughness. For Ti-6Al-4V+10 wt% Mo produced by PBF and DED processing, the

only mechanical property considered was the hardness. The commercial β -Ti alloy was not produced at high powers and high speeds, but rather at parameters that had already been used at the CSIR for the manufacturing of Ti-6Al-4V parts as a starting point.

Chapter 2: Literature review

2.1 Laser Technology

Since their invention over 50 years ago, the laser has found application in many different industries (Bretenaker *et al.*, 1966; Minerva, 2017). The construction industry uses lasers for surveying and building, for example defining a straight line on a horizontal plane in the construction of new homes and other buildings. In astronomy, the laser is used for monitoring geological motions on the earth by utilising the Lageos satellite, which sits in a stationary orbit over the earth. The retail industry uses the holographic method to read bar codes on labels on clothing and food sold. Also, the aerospace industry uses the laser gyroscope to detect stability and rotational motion of planes and rockets.

2.1.1 Types of high power lasers

Over the years, the laser has developed and different types of lasers have emerged. High power lasers such as CO₂ lasers, solid state lasers and diode lasers are of particular interest in manufacturing (Buchfink, 2007).

2.1.1.1 CO₂ gas lasers

The first CO₂ gas laser appeared in the United States in the 1970s. These lasers are based on a gas mixture, which is stimulated electrically. The laser beam quality determines the laser spot size and focus point. A wavelength of 10.6 μm , relatively high efficiency and a very good beam quality has made the CO₂ laser the most widely used laser type for material processing (Buchfink, 2007).

2.1.1.2 Solid state lasers

Instead of a gas, solid state lasers have a solid material as the active medium and were used on a fairly large scale for industrial productions in the early 1970s (Buchfink, 2007). In general, there are two classes of solid state lasers: continuous wave type which delivers a continuous output, and pulsed wave type which delivers a pulsed output achieved by pulsing the input energy.

Some solid state lasers use fibre optics which have the advantage of transportability without any quality or power losses (Buchfink, 2007). Solid state lasers include Nd:Yag lasers which have an yttrium-aluminium garnet as a gain medium and 1% neodymium ions as the dopant.

The Yb:Yag disc laser is doped with ytterbium and produces a better beam quality compared to the Nd:Yag laser (Buchfink, 2007). Also doped with ytterbium are Yb:Glass fibre lasers, which have a better plug efficiency (ratio: output laser power to consumed electrical power) of >30%, while the previously mentioned lasers have only managed 10% at best.

2.1.1.3 Diode Lasers

Diode lasers use a p-n semiconductor junction as a gain medium and even though the wall plug efficiency is greater than 40%, they are relatively strong and compact, but have a very poor beam quality. Despite this, and being used as pump sources for solid state lasers, they find application in soldering and hardening metals and welding of plastics where a very small spot size is not required (Buchfink, 2007).

2.2 Laser-based additive manufacturing

Today, lasers are known to be the solution to many problems in the manufacturing industry where they are used for drilling, cutting, cladding, welding, hardening and in additive manufacturing. The first process successfully carried out in laser manufacturing was laser drilling (Buchfink, 2007).

Initially, additive manufacturing was only used for the manufacturing of plastics, but it now accommodates the manufacturing of metals, which is far more relevant to the bulk of the manufacturing industry (Kruth *et al.*, 1998). The advantages of additive manufacturing include: saving time as the design can be easily changed on the CAD model, and complex geometries can be manufactured which would otherwise not be possible with conventional methods (Frazier, 2014).

Important processes in additive manufacturing are directed energy deposition (DED) and powder bed fusion (PBF) processes. These processes use the laser to melt metal powder, producing different layers joined together to form a component which was virtually designed in CAD and cut into 2D layers using a STL file in DED and in PBF (Kumar and Pityana, 2010).

2.2.1 Powder bed fusion process

The powder bed fusion (PBF) process is illustrated in Figure 2.1 (Kumar and Pityana, 2010), where the metal powder is spread onto a metal surface, the laser scans and melts the first layer. When it is done, the build piston moves down while the powder dispenser piston moves

up to enable the roller to deposit powder over the first layer which has been built by deposition and melting (Kumar and Pityana, 2010). When the powder is melted onto the previous layer, the surface of the previous layer is partially re-melted, producing columnar grains which are typical in parts produced using this method (Vilaro *et al.*, 2011). Easton *et al.* (2016) recognised that also contributing to the columnar structure is the suppression of nucleation which can occur when the magnitude of supercooling is reduced where high temperature gradients and high cooling rates exist. These columnar grains are responsible for the anisotropy in mechanical properties, and are preferential regions for crack propagation (Simonelli *et al.*, 2012a; Easton *et al.*, 2016). This process continues until the part is completed. The excess powder can be re-used as this process has minimal wastage, especially when compared to conventional methods.

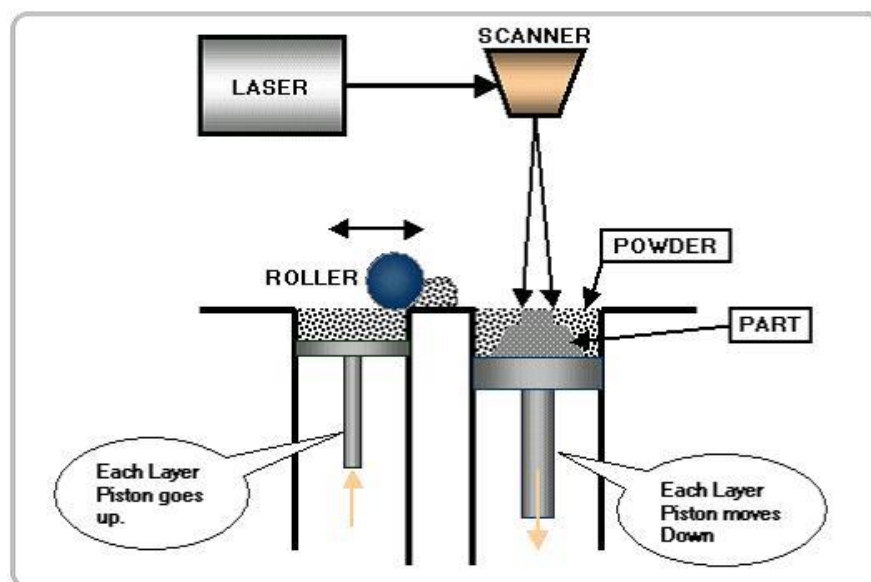


Figure 2.1: Schematic diagram of the PBF process (Kumar and Pityana, 2010).

The AeroswiftTM machine at the Council for Scientific and Industrial Research (CSIR) is one of the biggest PBF machines in the world. The machine was built at the CSIR-National Laser Centre at the CSIR in collaboration with Aerosud. The project started in 2011 and to date the machine has produced parts (throttle lever, a condition lever grip and a fuel tank pylon bracket) which have passed quality standards. It utilizes a combination of high power (up to 5kW) and high speed (up to 10 times faster than other commercially available machines) with a build envelope of 2000x600x600 mm³.

The solidification mechanism of powder bed fusion processes is similar to laser welding. High laser beam scanning speeds lead to short interaction times between the powder bed and the heat source. This results in fast heating and melting, causing shrinkage and circulation of molten metal, due to the temperature gradients and surface tension gradients (Kruth *et al.*, 2010).

Kruth *et al.* (2010) showed that the size and shape of the melt pool, heat-affected zone, transformation reactions and cooling rate are determined by the resulting heat transfer and molten flow (Figure 2.2). The grain growth and microstructure are influenced by the melt pool geometry.

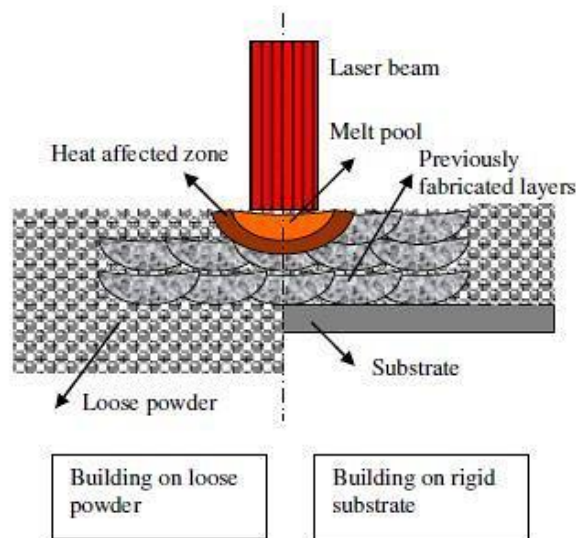


Figure 2.2: Schematic diagram showing different zones arising from processing (Kruth *et al.*, 2010).

2.2.2 Directed energy deposition

The DED process uses the same building blocks as laser cladding, and it can be used on a diverse range of materials. This is a blown powder method where a STL file of the part is used to develop a motion control program. This program is used to control the movement of the laser focal spot to outline all areas of the part on a substrate, layer by layer (Zhang *et al.*, 2007). Metal powder particles are injected into the laser focal zone and are melted, then re-solidified onto the previously-deposited fully solidified metal part which is trailing the moving molten pool created by the laser beam; this is shown in Figure 2.3 (Zhang *et al.*, 2007). After each layer, the powder nozzle and the focusing lens assembly move in the positive Z-direction perpendicular to the X-Y plane. Consequently, successive layers are built to produce the entire volume of the fused metal according to the CAD model.

Advantages of this process are that building can be done on 3D surfaces and on existing parts. This method is recommended for manufacturing of large parts and for refurbishments.

The PBF and DED processes are both considered for use in the aerospace industry with the DED process also finding wide usage in the making of implants in the medical industry. The main difference, besides the powder delivery method, is that higher powers and speeds can be achieved in the PBF process than in the DED process thus far. This then gives different microstructures and mechanical properties as different processing parameters are used.

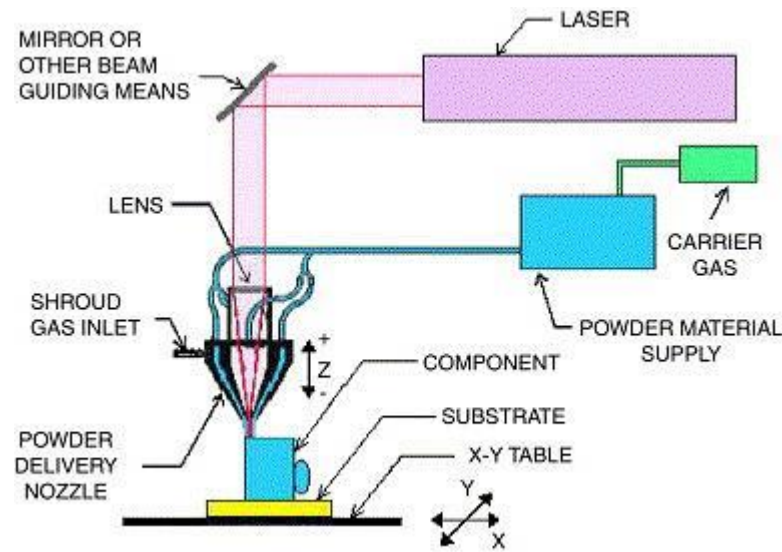


Figure 2.3: DED process (Zhang *et al.*, 2007).

2.2.3 Energy density

For both the PBF and the DED process, the energy density is an essential variable in determining the build quality and density of components (Attar *et al.*, 2014). The energy density (E) is defined by Equation 2.1 as the amount of energy supplied by the laser beam to a volumetric unit of powder material (Attar *et al.*, 2014).

$$E = \frac{P}{v \cdot h \cdot t}$$

Equation 2.1

where P is the laser power (in W), v is the laser scanning speed (mm/s), h is the hatch distance (mm) (the distance between two centres of overlapping tracks) and t is the layer thickness (mm).

The amount of energy supplied also influences the size and shape of the pores in the samples (Hao *et al.*, 2009). Excessively high energy density leads to spherical pores with diameters less than 50 μm , while insufficient energy densities leads to elongated, crack-like pores growing perpendicular to the build direction (Kasperovich *et al.*, 2016).

Chlebus *et al.* (2015) worked on alloying rhenium with titanium by PBF processes and found that increasing the energy density led to better dissolution of rhenium in titanium. Ficsher *et al.* (2016) also found this to be true when alloying niobium *in situ* with titanium by PBF processing.

2.3 Titanium and the titanium alloy Ti-6Al-4V

Titanium was first commercially produced in the 1950s, even though it was recognized as an element over 200 years ago (Jaffee and Promisel, 1968; RMI, 2015). It was used for high performance aircraft components in the airframe and jet engine. This was due to titanium's beneficial properties of light weight, high strength and structural efficiency. Today, the supply of feedstock ore for producing titanium is almost infinite, as it is the ninth most abundant element in the earth's crust and the fourth most abundant structural metal (Dept. of the Interior, 1953).

Titanium on its own has good properties, but when alloyed with other elements, a material suitable to almost any industry, especially the aerospace, chemical, industrial and energy industries, can be developed. These alloys have attractive mechanical properties, such as: high strength-to-density ratio, low density, excellent corrosion resistance and exceptional elevated temperature properties (Jaffee and Promisel, 1968; RMI, 2015). The Ti-6Al-4V alloy is one of the most widely used titanium alloys, especially in the aerospace industry, and was one of the first titanium alloys to be made when it was developed in the 1950s in the United States at the Illinois Institute of Technology (Jaffee and Promisel, 1968; Leyens and Peters, 2003). The success of this alloy is due to the good balance of mechanical properties and because it is the most extensively developed and investigated Ti alloy.

Pure titanium can exist in more than one crystallographic form, making it an allotropic element. At room temperature, it has a hexagonally close-packed α -Ti crystal structure (alpha phase) and at 883°C it transforms to a body-centred cubic β -Ti crystal structure (beta phase) (Molchanova, 1965; Donachie, 1988).

Figure 2.4 (Molchanova, 1965) demonstrates the influence of alloying elements on the crystal structure and the classification of titanium alloys. Adding elements such as aluminium and oxygen (α stabilising elements) increase the area of the α phase field to a higher temperature, while adding β stabilising elements (elements that display total solubility with beta titanium) such as vanadium and molybdenum lowers the β transus temperature, increasing the β phase field (Molchanova, 1965; Leyens and Peters, 2003). Beta stabilising elements (Figure 2.4C) have a much higher solubility in titanium compared to the β eutectoid elements (Figure 2.4D), such as iron and silicon.

2.4 Microstructure of Ti-6Al-4V parts produced via the PBF processes

As illustrated in Figure 2.5 (Donachie, 1988), above the β transus temperature, the microstructure consists of only β grains. When cooling takes place to the temperature where α and β coexist, α starts to nucleate along the prior β grain boundaries, forming grain boundary α . Leyens and Peters (2003) described the mechanism by which α nucleates in β to form the Widmanstätten structure. A β titanium's unit cell has six closest packed planes and six close packed directions that give a maximum of 12 variants of orientation where α can grow. The limited 12 possible orientations result in several repetitions of the orientation to form α lamellar packets. The radial spread of α lamellae during slow cooling is parallel to the $\{110\}$ planes of the β phase (Leyens and Peters, 2003; Vilane, 2013). With sufficient cooling rate, the lamellae will nucleate on the growth front of individual lamellae packets, in addition to nucleating on the grain boundaries.

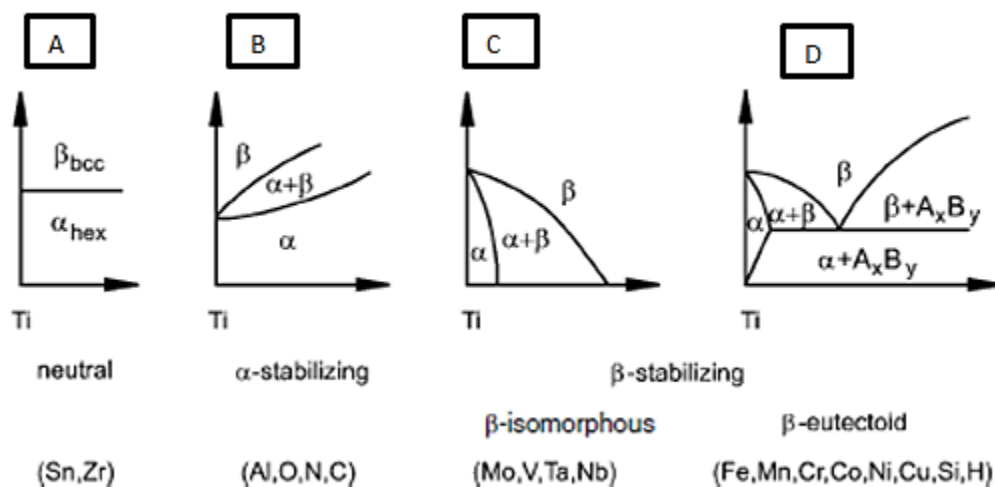


Figure 2.4: Influence of alloying elements on Ti alloy phase diagrams (Molchanova, 1965; Leyens and Peters, 2003).

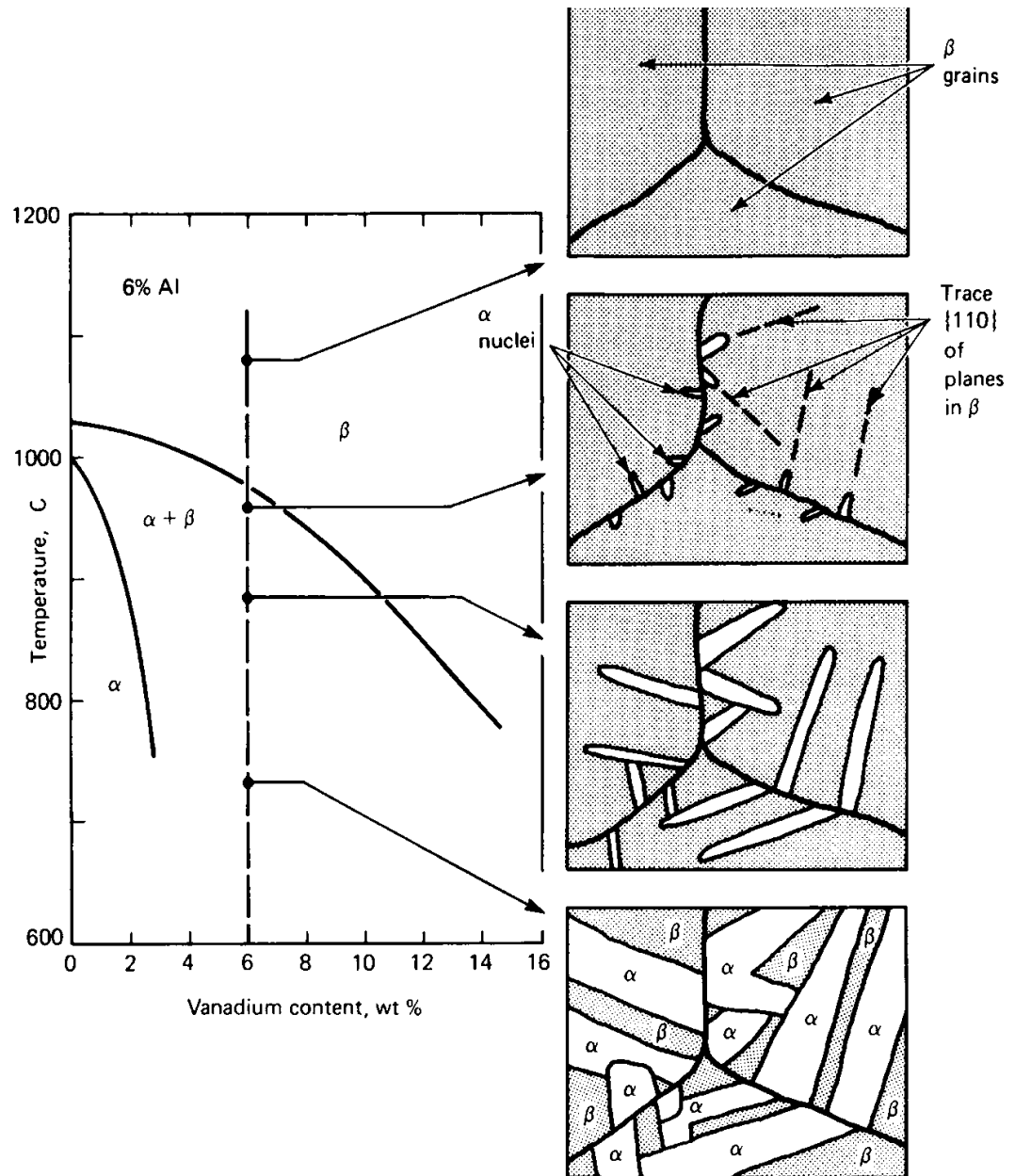


Figure 2.5: Microstructure evolution on cooling in Ti-6Al-4V from above the beta transus temperature (Donachie, 1988).

In laser powder-bed fusion processes, where very high cooling rates exist, a diffusionless process takes place. This transforms β to martensitic alpha, which can be α' (hexagonal crystal structure) or α'' (orthorhombic crystal structure). The α'' transformation is developed athermally or by a stress-assisted transformation, while the α' phase can only be formed by quenching from temperatures below $\sim 900^\circ\text{C}$ (Leyens and Peters, 2003; Gammon *et al.*, 2004).

Typical microstructural characteristics of laser-based additive manufactured metals include columnar grains, layered bands and martensite (Wu *et al.*, 2016; Vrancken *et al.*, 2014).

Components produced via the PBF process have a few problems. There are process related problems such as residual stresses. As a result of the microstructure, mechanical properties such as ductility and fracture toughness are compromised compared to those found in components produced via conventional methods (Figure 1.1).

2.4.1 Residual stresses

Residual stress is defined as the excess stress in mechanical parts in the absence of external stresses. Residual stress is a consequence of the metallurgical and mechanical history of each location in the part and the whole part during the manufacturing process.

Most manufacturing processes induce residual stresses which influence mechanical properties such as fatigue resistance and fracture toughness and also affect the component's structure. Therefore, understanding the role of residual stresses in mechanical parts is imperative, especially because the failure of a component is not only due to external loads. Residual stresses introduced into a component via the manufacturing process can have a positive effect, like increasing the fatigue limit when surface compressive stress is involved and it can have a negative effect like decreasing the stress corrosion behaviour of a component when tensile residual stress is involved (Totten *et al.*, 2002).

There are a number of factors that can generally induce macroscopic residual stress (Totten *et al.*, 2002):

- Heterogeneous plastic flow as a result of external treatment, e.g. shot peening,
- Heterogeneous plastic deformation during variable heating or cooling, e.g. quenching,
- Heterogeneity of a chemical or crystallographic order, e.g. case hardening,
- Structural deformation from metalworking, e.g. heat treatment, surface treatments e.g. chrome plating, and
- Differences in coefficients of thermal expansion and differences in deformability of the different components of composites.

Table 2.1: Origins of residual stress resulting from various manufacturing processes (Totten *et al.*, 2002).

Process	Mechanical	Thermal	Structural
Casting	No	Temperature gradient during cooling	Phase transformation
Shot peening, hammer peening, roller burnishing, laser shock treatment, bending, rolling, chasing, forging, straightening, extrusion	Heterogeneous plastic deformation between the core and surface of the part	No	Depends on the material
Grinding, turning, milling, drilling, boring	Plastic deformation due to the removal of chips	Temperature gradient due to heating during machining	Phase transformation during machining if the temperature is sufficiently high
Quenching without a phase transformation	No	Temperature gradient	No
Surface quenching with a phase change (induction, EB, laser, plasma, classical methods)	No	Temperature gradient	Change of volume due to a phase change
Case hardening, nitriding	No	Thermal incompatibility	New chemical component with volume modification
Welding	Shrinkage	Temperature gradient	Microstructural change (HAZ)
Brazing	Mechanical incompatibility	Thermal incompatibility	New phase at interface
Electroplating	Mechanical incompatibility	Mechanical incompatibility	Composition of plating depending on bath used
Thermal spraying (plasma, laser, HVOF)	Mechanical incompatibility, microcracking	Thermal incompatibility, temperature gradient	Change of phase in plating
PVD, CVD	Mechanical incompatibility	Mechanical incompatibility	Change of phase
Composite	Mechanical incompatibility	Mechanical incompatibility	No

EB, electron beam; HVOF, high-velocity oxygen fuel; HAZ, heat-affected zone

The additive manufacturing process is similar to the welding process. Table 2.1 (Totten *et al.*, 2002) highlights that residual stress originates from mechanical effects, e.g. shrinkage, thermal effects such as thermal gradients and from structural changes such as the change in microstructure in the heat affected zone. In terms of powder bed fusion processes, the short interaction times and highly localized heat input induce large thermal gradients during processing. These generate a build-up of thermal stresses which lead to deformation of parts, delamination and cracking during manufacturing and in addition, when removing the sample from the base plate, distortion and cracking may occur. The development of non-equilibrium phases and the segregation phenomena results from the rapid solidification (Zhirnov *et al.*, 2015). The residual stress works over larger dimensions when building larger parts, making these parts more prone to this type of failure.

Vrancken *et al.* (2013) discussed the correlation between material properties and stress. They stated that the development of large thermal gradients is more common in materials with low thermal diffusivity. Due to their high heat capacities and their low thermal conductivity, these materials retain heat, instead of conducting it away (Vrancken *et al.*, 2013), subsequently giving the large thermal gradients in the part and hence large residual stresses.

2.4.2 Mechanical properties

Although there are desirable mechanical properties arising from the acicular α' martensitic microstructure, such as high hardness and strength, there are problems which arise, such as the fact that martensite favours intergranular cracking, resulting in brittle failure. The acicular α' microstructure is strongly textured, resulting in significant anisotropic behaviour, causing a large inconsistency in the mechanical response under external loading along various sample orientations (Xu *et al.*, 2015). Other mechanical properties associated with this microstructure are low fracture toughness and ductility.

Ductility is defined as a metal's ability to plastically deform under stress (Damkroger *et al.*, 1988). Parts produced by laser-based additive manufacturing are usually characterized by high yield stress, high ultimate tensile strengths and relatively low ductility of less than 10% (Vrancken *et al.*, 2012). For the additive manufacturing of parts for the aerospace industry, the lack of ductility is a problem, especially for large parts, since they are more prone to cracking.

Fracture toughness is another important property which is generally low in additively manufactured parts. Fracture toughness is a measure of the ability of a material to resist crack

propagation (Bolton, 2000). Due to the high internal stresses which exist during laser processing, there is a high probability of cracks forming. Although cracks also form in smaller parts under the same conditions used in the manufacturing of larger parts, they tend to propagate to failure in large parts. Defects such as cracks, voids, weld defects and metallurgical inclusions are known to be stress raisers, and can act as crack initiation sites (Bolton, 2000). Due to this, the processing parameters must be closely controlled such that minimal defects form, because they adversely affect ductility and fracture toughness. The high stresses present in parts during processing are dependent on the absolute size of the part. Figure 2.6 (NDT, 2016) illustrates that the stress state next to the defect changes with the thickness of a part (B) until a critical dimension is reached. The fracture toughness decreases with increasing part thickness, leading to the lower fracture toughness in larger components.

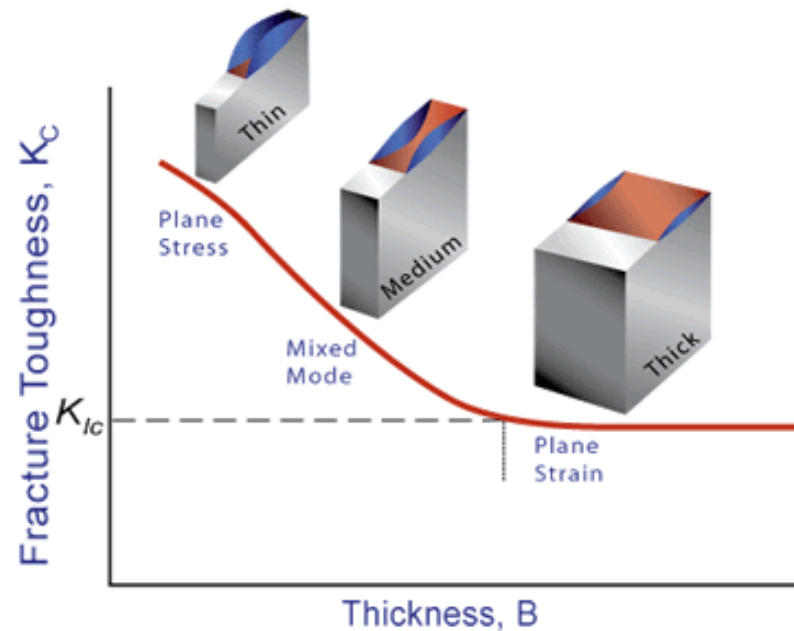


Figure 2.6: Relationship between fracture toughness and thickness of specimen, where blue colour is plane stress and red is plane strain (NDT, 2016).

2.5 Fundamentals of *in situ* alloying

In situ alloying occurs when the alloying process takes place during the processing/manufacturing stage in additive manufacturing (Dongdong, 2015). With regards to directed energy deposition (DED), this is more practical and the process gives better control compared to powder bed fusion processes. Other advantages of *in situ* alloying using the DED process include cost savings associated with eliminating the production steps for making pre-alloyed

powders, manufacturing of compositionally graded materials and utilization of less laser energy due to the availability of reaction generated heat (Dongdong, 2015).

2.5.1 *In situ* alloying via blown powder methods

In situ alloying via DED process is achieved by feeding elemental powders from two powder feeders; these powders are then fed to a single pipe which is connected to the feeding nozzles where they are melted by the laser onto the substrate, as depicted in Figure 2.7 (Study blue, 2017).

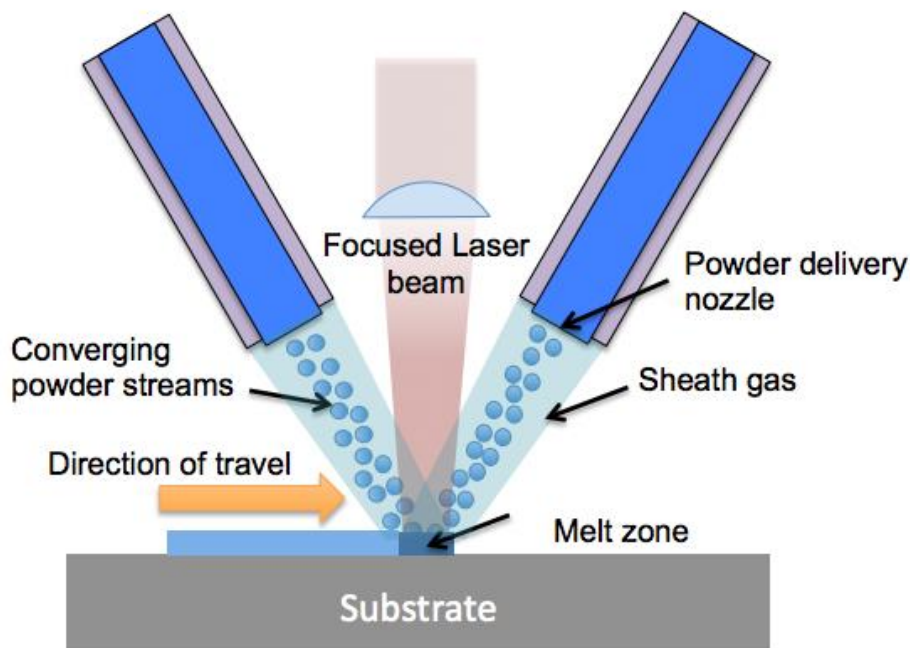


Figure 2.7: Directed energy deposition schematic (Study blue, 2017).

The homogeneity of *in situ* alloying of intermetallic compounds is established by the rapid exothermic reactions which are involved during formation of intermetallics (Study Blue, 2017). As a result of two powder feeders being used, the microstructure and phases formed can be controlled with the build direction by regulating the ratios at which the different powders are fed. The laser engineered net shaping (LENS) system is a blown powder method which can be used for *in situ* alloying. Collins *et al.* (2003) used LENS to manufacture compositionally graded Ti-V and Ti-Mo alloys. The Ti-Mo alloy (Figure 2.8) at low Mo content (<1 at.%) yielded a microstructure consisting of Widmanstätten α laths with a small volume fraction of β at the lath boundary (Collins *et al.*, 2003; Almeida *et al.*, 2012).

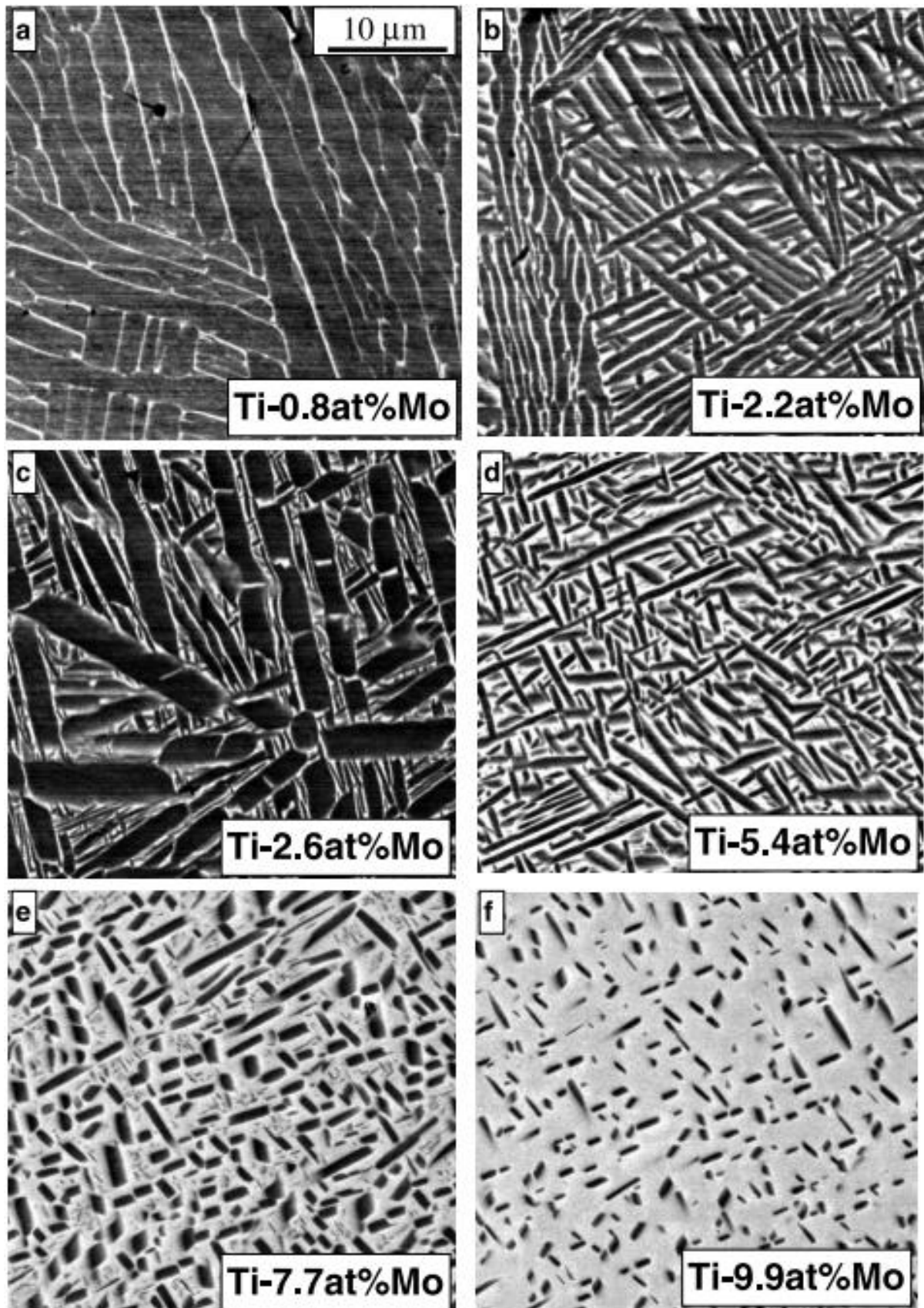


Figure 2.8: SEM images of LENS deposited Ti-xMo graded alloys (Collins *et al.*, 2003).

As the Mo composition increased, there was a decrease in the width of the α laths and conversely an increase in the volume fraction of β . It was also observed that the relatively longer and wider laths seemed to split into shorter precipitates. At 9.9 at.% Mo, the microstructure largely consisted of β -Ti with a small volume fraction of finely distributed α precipitates. In terms of hardness, as the Mo content increased, there was an initial increase until a peak value (10 at.% Mo) was reached and then the hardness showed a decreasing trend. Collins *et al.* (2003) reported no unmelted particles.

2.5.2 *In situ* alloying via powder bed fusion processes

For powder bed fusion processes, pre-mixing (blending) or pre-alloying (milling) needs to be done before processing.

2.5.2.1 Powder mixing

In order to ensure proper blending, the two powders to be mixed should have different shapes and particle sizes, so that the smaller powder sits in the spaces between the larger particles, as shown in Figure 2.9 (Vrancken *et al.*, 2014). Vrancken *et al.* (2014) used Mo powder which was small and irregular compared to the Ti-6Al-4V powder. Similarly, Fischer *et al.* (2016) used a smaller size of niobium powder while mixing it with Ti-6Al-4V powder. They also noted that the differences in melting temperatures of the two materials (Nb having a much higher melting temperature) would ensure better diffusion of Nb into Ti.

Powder mixing is often used in powder bed fusion processes for *in situ* alloying, although there are a few areas of concern such as homogeneity and repeatability (Chlebus *et al.*, 2015; Fischer *et al.*, 2016; Kinnear *et al.*, 2016). The smaller particles may segregate to one area, affecting the degree of homogeneity of the mixture.

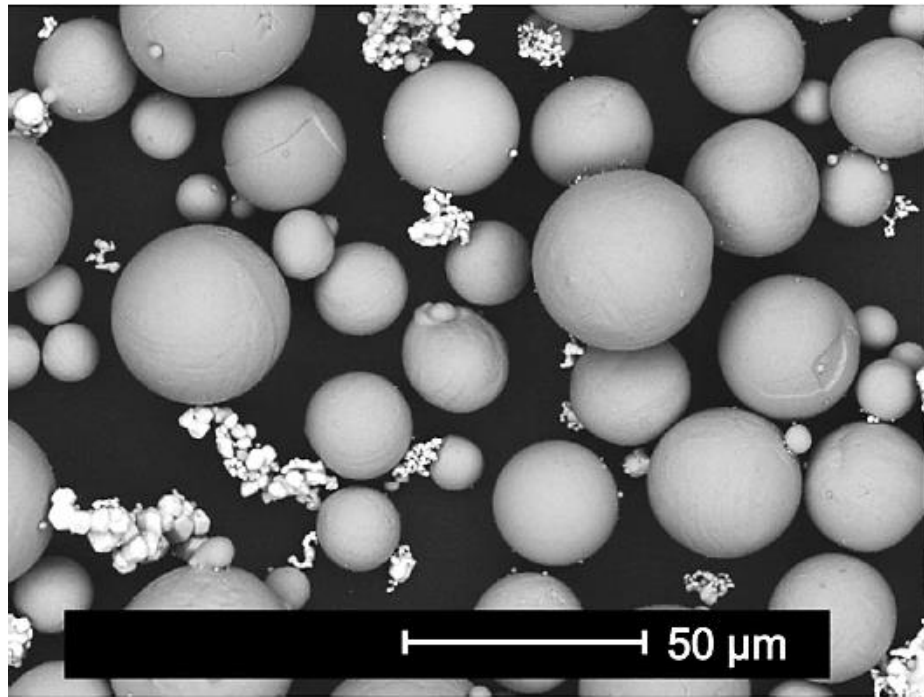


Figure 2.9: SEM BSE image of blended powder (Vrancken *et al.*, 2014).

2.5.2.2 Microstructure of material alloyed *in situ* via PBF

The microstructure of material alloyed *in situ* via powder bed fusion processes (Figure 2.10) is different from that obtained in DED processes (Figure 2.8) due to the faster speeds used in PBF. When Vrancken *et al.* (2014) added 10 % Mo to Ti-6Al-4V, the resultant microstructure consisted of a β titanium matrix with scattered pure Mo particles (Figure 2.10A). Compared to Ti-6Al-4V, they found an increase in fracture strain from 7.3 to 20.1% and fracture toughness, accompanied by a reduction in ultimate tensile stress from 1267 to 919 MPa).

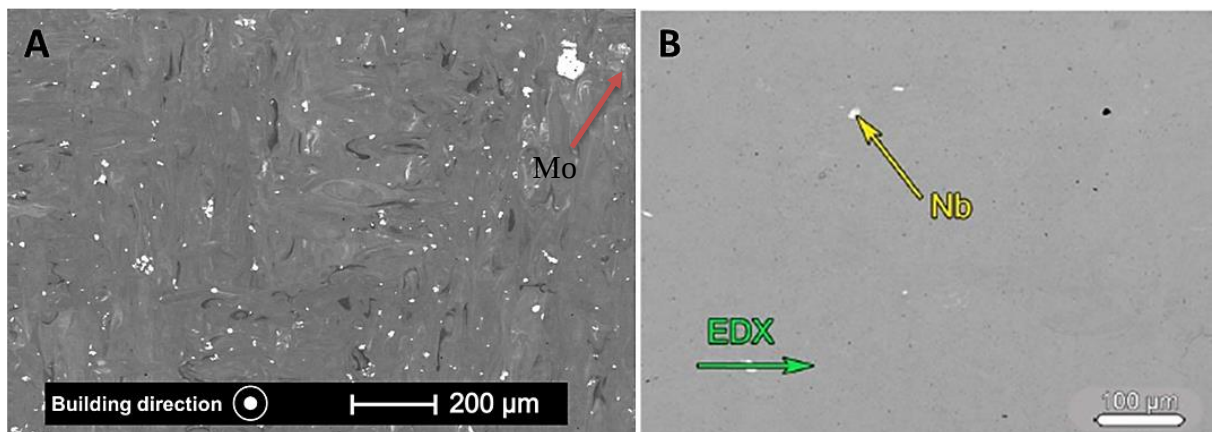


Figure 2.10: SEM (BSE) images of composite microstructures where A is that of Ti-6Al-4V and 10% Mo (Vrancken *et al.*, 2014) and B is that of Ti and 26% Nb (Fisher *et al.*, 2016).

Fischer *et al.* (2016) added 26 wt % niobium to titanium for biomedical applications such as joint replacements. They reported a relatively homogeneous microstructure with unmelted Nb particles making up less than 1% of the total Nb mass in the alloy (Figure 2.10B). This was only possible when a laser energy density of more than 200J/mm^3 was used. There was also micro-segregation at the melt pool boundaries. This chemical heterogeneity was attributed to the remelting-resolidification of the previously deposited layer, although it had no effect on the overall grain structure.

Chlebus *et al.* (2015) added different quantities of rhenium to titanium for selective laser melting, with the objective of raising the hardness and strength, as well as the recrystallization temperature of titanium. Rhenium, like molybdenum and other refractory metals or compounds, readily dissolves in molten titanium (Chlebus *et al.*, 2015). In the superheated state, liquid titanium is especially chemically reactive. They found that even the lowest accepted scanning speed of 24mm/s was not sufficient for complete dissolution of rhenium particles in molten titanium. Consequently, 10-15 vol.% of the rhenium particles were left undissolved. The general microstructure was lath type or acicular-type martensite. Conversely to the addition of Mo and Nb, the addition of Re reduced the ductility of Ti-Re components (Chlebus *et al.*, 2015).

To improve the relatively poor wear resistance and low hardness of Ti-based alloys, ceramic reinforcements such as titanium boride can be added (Attar *et al.*, 2014). They pre-alloyed Ti and TiB_2 by using a ball mill for PBF processing.

2.6 Galvanic corrosion

Many benefits have been identified from alloying of Ti-6Al-4V *in situ* with Mo, such as improvement in mechanical properties like ductility and fracture toughness. The resultant (composite like) as-built microstructure (Figure. 2.10A) gave rise to concerns around the micro-galvanic corrosion resistance of such a microstructure. This topic has not been reported by other researchers in the field, including Vrancken *et al.* (2014) and Fisher *et al.* (2016).

Galvanic corrosion results from the contact between two different conducting metals in a corrosive environment (Hack, 1988; Zhang, 2011). This type of corrosion is mostly found in ships where the parts immersed in the sea water are made of various metal alloys, or more relevant to the current topic, in a metal matrix composite material, where reinforcing material is spread throughout the metal *e.g.* graphite (Zhang, 2011). Galvanic corrosion may result in

the accelerated deterioration of one metal or the corrosion protection of a connected metal, known as cathodic protection (Zhang, 2011). Galvanic corrosion is not only affected by the potential difference between the two metals in contact. Some other metallurgical factors such as: surface conditions, electrolyte properties, reactions, environmental effects, and geometric factors also play a role, as shown in Figure 2.11 (Zhang, 2011).

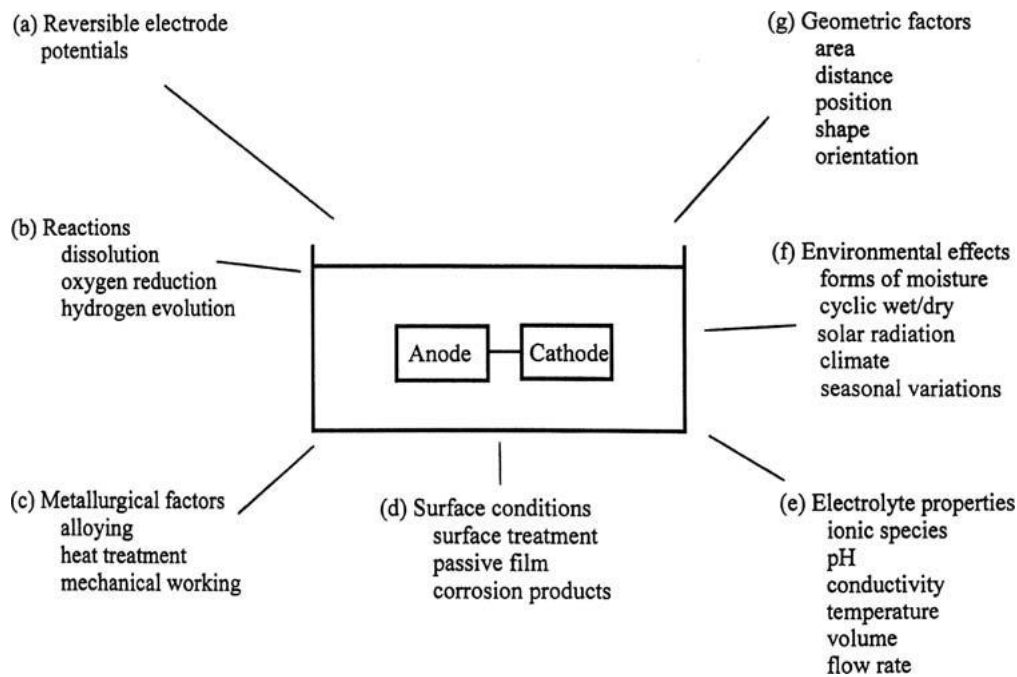


Figure 2.11: Factors included in bimetallic corrosion (Zhang, 2011).

The inherent polarity of a galvanic couple is determined by the reversible electrode potentials, while the actual polarity depends on the reactions, surface conditions and metallurgical factors such as alloying and heat treatment (Zhang, 2011). Geometric factors such as area, distance between the different areas, shape, position and orientation, make galvanic corrosion unique and more complex compared to other forms of corrosion which are only affected by the material and the environment (Zhang, 2011). An important factor under geometrical factors is area, mainly focusing on the anode and cathode areas.

The area ratio needs to be considered when looking at the possibility of having galvanic corrosion between two metals (NPL, 2007). In the case where the area of the cathode is larger than the area of the anode (Figure 2.12B), oxygen is easily reduced, thereby increasing the galvanic current and therefore there is an increase in the corrosion (NPL, 2007). There will

be insignificant corrosion attack in the case where the anode area is larger than the cathode area (Figure 2.12A). When the corrosion current relies on the dissolved oxygen diffusion rate to the cathode (static conditions), the corrosion attack will be proportional to the area of the cathode and will not be dependent on the size of the anode according to the catchment area principle (NPL, 2007).

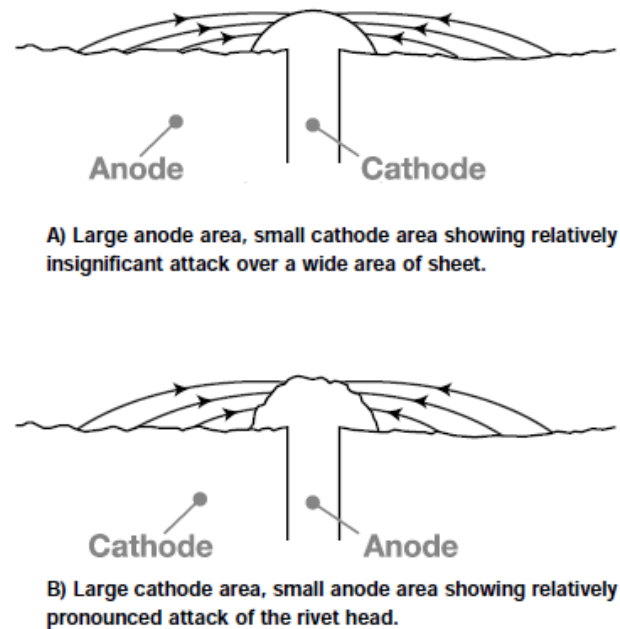


Figure 2.12: Dependence of Galvanic corrosion on area (NPL, 2007).

Referring to the galvanic series under sea water conditions (Appendix A), Ti-6Al-4V is number 85 while Mo is number 58; therefore, the contact between these two dissimilar metals is conducive for galvanic corrosion in the right environment. The difference in the potentials between the two metals means that in an electrically conducting corrosive solution/liquid, the current will flow from the more electronegative anode (Mo in this case) to the more electropositive cathode (Ti-6Al-4V). This will result in the corrosion of the anode.

It is also important to note that from the microstructure, the area of the anode is relatively smaller than the area of the cathode; this is expected to increase the corrosion rate according to the 'area ratio'. Micro-galvanic corrosion of Molybdenum particles could hinder the usage of this composite in the as-built state for a number of applications, like the aerospace industry.

2.7 Modification of Ti-6Al-4V microstructure

Ductility can be improved in different ways, and for conventional methods such as casting, Luan *et al.* (2014) found that micro-alloying with boron improved ductility and changed the fracture mode from intergranular to transgranular fracture. The improvement in ductility was found to be related to the grain refinement of the prior beta grains, which can also improve properties such as strength, fatigue resistance, fracture toughness, corrosion-fatigue resistance and corrosion resistance.

The reduction of the prior β grain size resulted in the shortening of α laths, thereby decreasing the size of α colonies (Pederson *et al.*, 2012). Luan *et al.* (2014) and Pederson *et al.* (2012) confirmed the earlier work of Pederson (2002), stating that decreasing the α colony size meant decreasing the measure of slip (slip length), leading to an increase in yield strength, ductility, crack propagation resistance and crack nucleation resistance, while increasing α colony size only leads to improved macro-crack propagation resistance and fracture toughness (Pederson, 2002).

The β phase is more ductile than the α phase. Therefore, stabilising β by adding elements such as molybdenum, vanadium, tantalum and niobium leads to an increase in ductility (Leyens and Peters, 2003). The amount of these elements must be carefully monitored, as increasing ductility mostly leads to a decrease in strength. Vrancken *et al.* (2014) found that the addition of 10 wt% molybdenum changed the solidification mode from planar to cellular, as a result of severe solute distribution between the liquid and the solid. Planar solidification takes place when there is a combination of high actual temperature gradient (G) and low growth rate (R), while cellular growth has a higher growth rate compared to the planar solidification but lower temperature gradient.

The microstructure of Ti-6Al-4V alloyed with Mo (β titanium matrix with unmelted Mo Figure 2.10A) was possible due to the ability of Mo to suppress the β phase from transforming to acicular martensite during fast cooling and hence fully retaining the β phase. Vrancken *et al.* (2014) also found that static tensile properties showed a combination of reduced UTS and increased fracture strain compared to Ti-6Al-4V, as shown in Figure 2.13.

Post heat treatment of Ti-6Al-4V has also been found to reduce residual stresses and increase ductility by refining the microstructure of parts produced by laser based additive manufacturing. Xu *et al.* (2015) showed that low temperature ageing for at least 4-8 hours

resulted in a microstructure of fine lamellar alpha and beta, with or without primary alpha. This was possible due to the decomposition of α' martensite during ageing.

Other problems arising from the processing include the development of pores, which are process induced defects from initial powder contamination, and local voids after powder layer deposition and when non-ideal scan parameters are used (Simchi *et al.*, 2003). Current solutions to the porosity problem include hot isostatic pressing and laser re-melting, which increase the production time and cost (Simchi *et al.*, 2003). Low surface quality can be improved by laser re-melting of the outer layer.

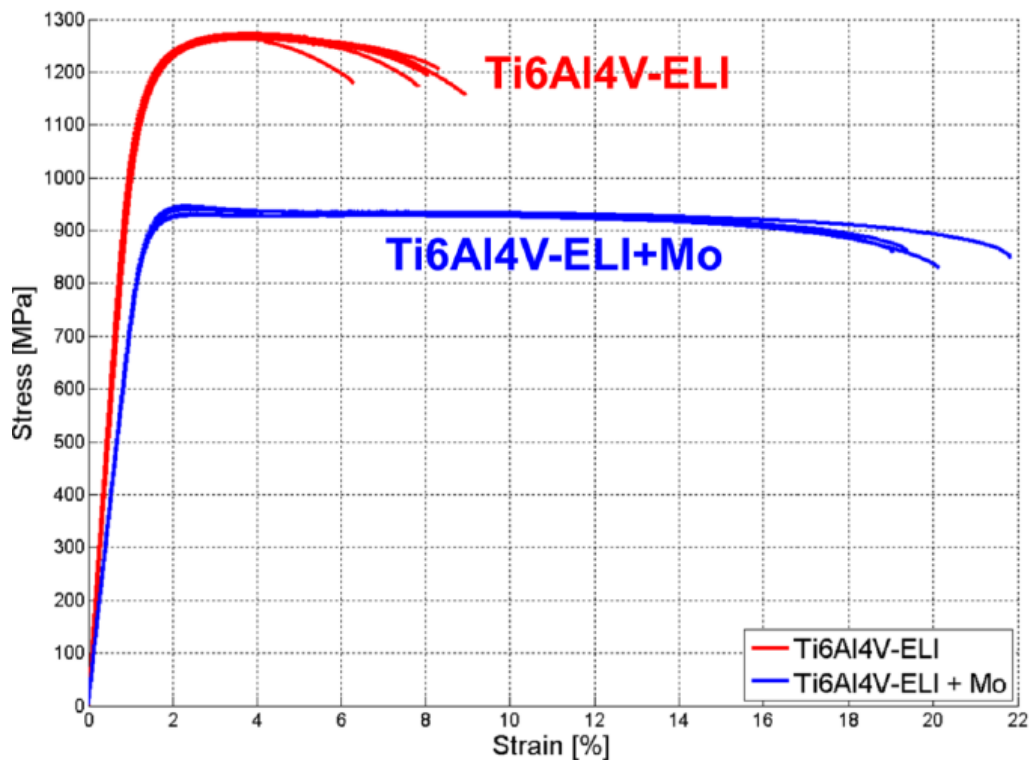


Figure 2.13: Stress-strain curves for SLM produced Ti-6Al-4V and wrought Ti-6Al-4V (Vrancken *et al.*, 2012).

2.8 QuesTek Innovations LLC

QuesTek Innovations LLC was founded by Prof. G. Olson and Mr R. Genellie in 1997. They are a global company and leader in integrated computational materials engineering (ICME) and their business model involves designing, developing and patenting new materials and licensing to producers, OEMs and End-users. QuesTek has won awards for seven US patents with 23 US patents pending and they have at least 35 ongoing materials-focused projects (QuesTek, 2016). The company is known for its success in designing alloys to meet

designated performance requirements, commercialising these alloys and then qualifying and developing them for demanding applications in aerospace and other industries. This is done by incorporating suitable thermodynamic and kinetic databases with advanced computational modelling tools, so that the explicit chemical compositions and important processing parameters of a material can be accurately and quickly determined.

The ICME technologies used by QuesTek are accepted as the best alternative to traditional, empirical, trial-and-error methods of material discovery, saving time and money associated with novel materials development (QuesTek, 2016). With regard to additive manufacturing (AM), and the increased interest in developing new alloys to suit the manufacturing process, QuesTek has developed a modified Ti-6Al-4V alloy. This was done by considering the rapid heating and cooling rates which lead to intense residual stresses, non-equilibrium microstructures, hot tearing and quench suppressibility concerns. This was done using advanced ICME technology. In addition, oxygen tolerance and novel precipitation strengthening concepts were also studied.

The QuesTallo alloy, with composition given in Table 2.2 (Wright *et al.*, 2011), was patented in 2011 in Europe and Japan, with its status still pending in the United States. QuesTallo was found to have better fracture toughness and ductility compared to wrought Ti-6Al-4V and was more suited for AM processes.

Table 2.2: QuesTallo composition (Wright *et al.*, 2011).

Element	Composition (wt%)
Aluminium	~3.0 - ~6.0
Tin	~0 - ~1.5
Vanadium	~2.0 - ~4.0
Molybdenum	~0.5 - ~4.5
Chromium	~1.0 - ~2.5
Iron	~0.2 - ~0.55
Oxygen	~0 - ~0.35
Boron	~0 - ~0.007
Other incidental elements	~0 - ~0.6
Titanium	Balance

2.9 Rationale for the current study

In light of the current importance of alloy development in additive manufacturing, especially for finding material with better mechanical properties than Ti-6Al-4V processed by PBF, *in situ* alloying would be a faster and more convenient way of developing alloys if the process could produce a homogeneous microstructure (Seifi *et al.*, 2016). Work has been successfully completed on *in situ* alloying Ti-6Al-4V with Mo in order to improve the fracture toughness and ductility by stabilizing the β phase (Vrancken *et al.*, 2014), although the power and the speeds used in that work are moderate compared to the speeds used by the AeroswiftTM machine at the CSIR. Obtaining the same effect for high power, high speed application would mean that alloys with better mechanical properties could be developed during processing, saving time and money.

It is also worthwhile to compare the implications of alloying through the PBF and the DED process. This would give an indication of which process is capable of producing a homogeneous microstructure. The as-built composite microstructure of Ti-6Al-4V and 10 wt% Mo alloyed *in situ*, produced by Vrancken *et al.* (2014) via PBF process has unmelted Mo particles which may not be acceptable in industries with stringent requirements such as the aerospace industry. Another implication of a composite microstructure is micro-galvanic corrosion, which if environmentally conducive can decrease the life span of the component.

In order to cover the full topic, it is of interest to investigate whether the route of *in situ* alloying of Ti-6Al-4V with Mo to produce a fully β alloy is more beneficial than using a commercial β -Ti alloy powder such as Ti-3Al-8V-6Cr-4Zr-4Mo for additive manufacturing.

Chapter 3: Experimental procedure

3.1 Materials

The titanium alloy Ti-6Al-4V (with two different particle size ranges) was procured from TLS Technik Spezialpulver in Germany. The first powder had a particle size of 45-100 μm (Section 3.2.1) and the second powder (with a smaller particle size) had a size range of 20-60 μm . Molybdenum, also having two different particle size ranges, was obtained from Weartech in South Africa. The Mo powder used for the powder bed fusion (PBF) process consisted of particle sizes of less than 32 μm . The particle size of Mo used was finer than that of Ti-6Al-4V for the purpose of obtaining better melting of Mo by increasing the particle surface area. The Mo used with a LENSTM machine had a particle size ranging from 45-100 μm due to its powder particle size requirements, for good powder flowability. Due to the difficulty of getting commercial titanium β alloys as powder, a Ti-3Al-8V-6Cr-4Zr-4Mo rod was procured from Titanium A-Z South Africa and exported to Germany for gas atomization at TLS Technik Spezialpulver. The particle size of this alloy was less than 112 μm .

3.2 Powder mixing and Characterization

3.2.1 Purpose of mixing powders

Mo powder was mixed with Ti-6Al-4V powder as a means to create a homogeneous mixture to be used during PBF processing and the DED process.

3.2.2 Powder mixing

100 g of Mo powder was mixed with 900 g of Ti-6Al-4V powder in a Turbula mixer (System Schatz, made in Switzerland) to make 1 kg of mixed powder for processing on each machine (SLM and LENSTM), described in more detail in Sections 3.3.1 and 3.3.2 respectively. Each powder mixture was mixed for 30 minutes at 75 rpm.

3.2.3 Powder characterization

Powder particle size analysis of the mixed powder and the titanium beta alloy was conducted at the Material Science and Manufacturing (MSM) unit at the Council for Scientific and Industrial Research (CSIR). A Microtrac Bluewave particle size analyser was used to analyse

the particle size distribution. A JEOL JSM-6010PLUS/LA Scanning Electron Microscope (SEM) was used to analyse the particle morphology.

3.3 Sample manufacturing

Figure 3.1 shows the different types of experimental samples produced for this work. With a selective laser melting (SLM) machine (PBF), high power (2-3 kW) and low power (<2 kW) samples were built at high speeds of 2-4 m/s. The samples built at low powers were those of the β alloy Ti-6Al-4V+10 wt% Mo alloyed *in situ* and the commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo), while the samples built at high powers were that of Ti-6Al-4V and the β alloy Ti-6Al-4V+10 wt% Mo alloyed *in situ*. Only tensile samples were built for low power, high speed tensile Ti-6Al-4V samples for comparison with the β -Ti alloy. This was because the initial plan was to build high power, high speed samples for the commercial β -Ti alloy and compare with the high power, high speed Ti-6Al-4V samples. However, this was not possible due to the malfunction of the larger spot size fibre (480 μ m) (capable of building at high powers) before the manufacturing of the β -Ti alloy samples. Therefore, Ti-6Al-4V samples could not be built at low powers. With a LENSTM machine (DED) only low power (300-400 W) and low speed (0.0085-0.0106 m/s) samples were built *in situ* using Ti-6Al-4V+10 wt% Mo. This was done after seeing the microstructural effects arising from using high speeds offered via PBF processing.

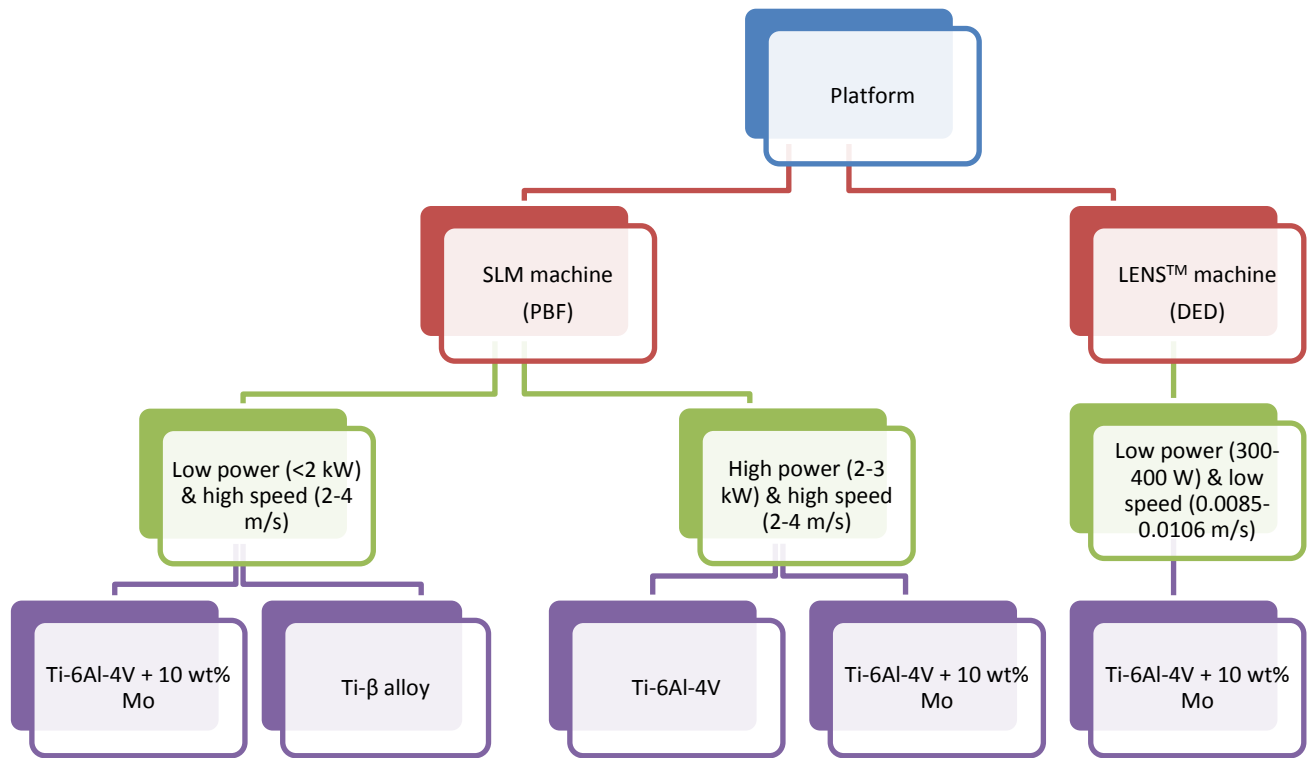


Figure 3.1: Summary of experiments done in both the SLM (PBF) and LENSTM (DED) machines.

3.3.1 Manufacturing on the SLM Machine (powder bed fusion)

Figure 3.2 shows the SLM machine used in this study. This machine was built in-house, *i.e.* it is not a commercially purchased machine. This SLM machine is smaller than the AeroswiftTM machine but offers identical processing conditions (laser power, speed, atmosphere and scraping mechanisms), therefore it is mostly used for process development purposes. Before operation, the system was purged to remove all oxygen from the chamber, and it was then filled with argon.

An oxygen sensor was used to monitor the environment in the chamber throughout the purging process and the manufacturing of samples. After the oxygen reached below 1000 ppm, processing began with the scraper depositing a thin layer of powder on to the base plate and then moving back to its home position. The scanner then marked the base plate in the pattern of the CAD drawing provided to the system. After the marking, the base plate moved down the same distance as the layer thickness and the scraper deposited another layer of powder. This process continued until the samples were completed. With the SLM machine 10 x 10 x 10 mm³ samples were built for the purposes of microscopic analysis (Figure 3.3a).

Rectangular samples $56 \times 12 \times 6 \text{ mm}^3$ samples were built from Ti-6Al-4V and the β -Ti alloy for tensile testing (Figure 3.3b).

3.3.1.1 SLM (low power, high speed)

The first samples manufactured from the mixed powder (Ti-6Al-4V+10 wt% Mo) on the SLM machine were made using the smaller size Ti-6Al-4V powder (20-60 μm), which is the preferred particle size for the machine as outlined by the CSIR-National Laser Centre, and Mo powder with a particle size of 20-60 μm (Table 3.1). Parameters such as power and hatch overlap (degree of which one track overlaps on top of the other) were kept constant in the manufacturing of samples alloyed *in situ* and only the speed was varied. This was due to the speed being identified (Chlebus *et al.*, 2015) as one of the major parameters that would influence the dissolution of Mo, therefore its effects needed to be investigated.

The beta alloy samples were manufactured using standard parameters currently used for Ti-6Al-4V (Table 3.2). These samples were manufactured using a 250 μm spot size. Utilizing a fibre with a larger spot size of 480 μm would be beneficial for reaching higher powers, but this fibre was not available at the time of conducting the experiments. These samples were made to evaluate the feasibility of manufacturing a β -Ti alloy *in situ*. The commercial β titanium alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) was therefore also evaluated to compare the *in-situ* and the commercial beta alloys.

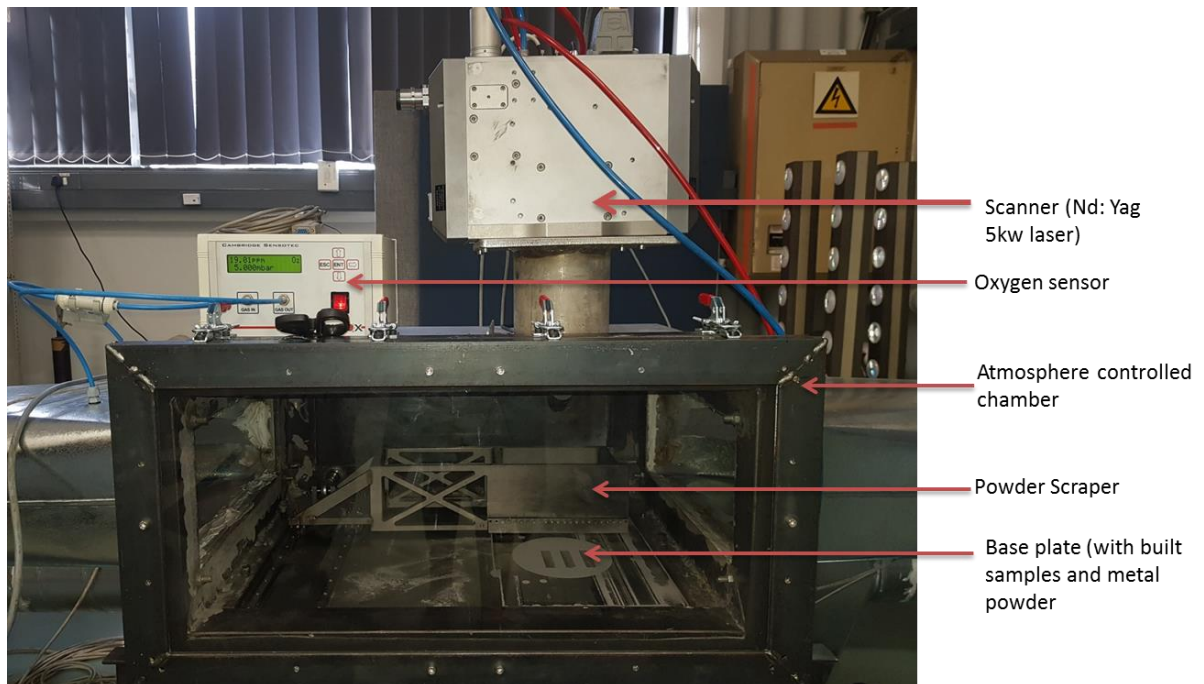


Figure 3.2: Photograph of the SLM machine.

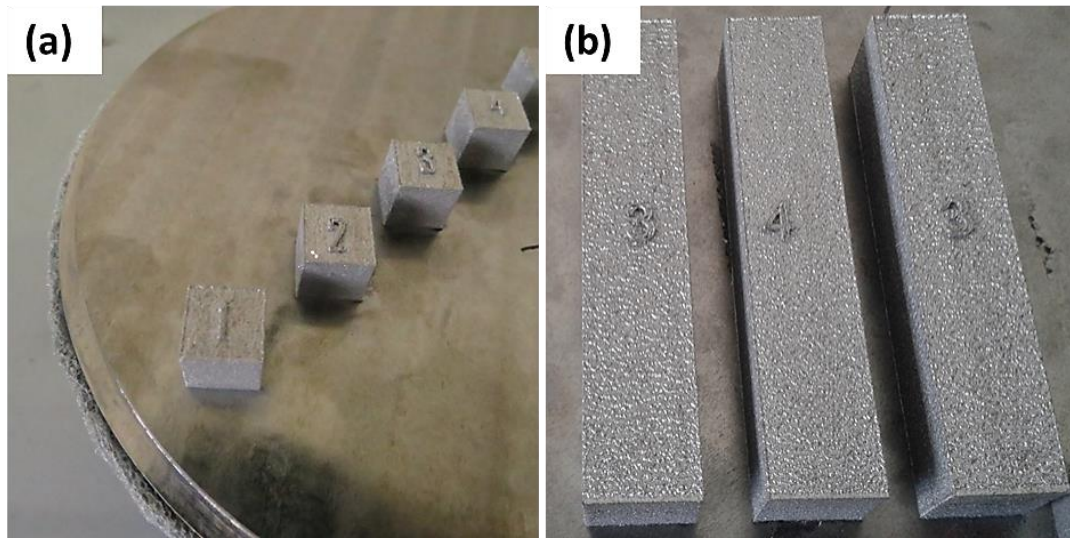


Figure 3.3: Samples built on a SLM platform: (a): 10x10x10 mm³ squares for microstructural analysis, (b) 56x12x6 mm³ rectangular samples for tensile testing.

Table 3.1: Experimental matrix for Ti-6Al-4V + 10 wt% Mo samples: SLM machine, low power, high speed.

Sample ID	Power (kW)	Speed (m/s)	Hatch overlap (%)	Energy density (J/mm ³)
A	1.3	2	50	104
B	1.3	2.5	50	83.2
C	1.3	3	50	69.3
D	1.3	3.5	50	59.4
E	1.3	4	50	52

Table 3.2: Experimental matrix for Ti-beta alloy samples: SLM machine, low power, high speed.

Sample ID	Power (kW)	Speed (m/s)	Hatch overlap (%)	Energy density (J/mm ³)
1	1.3	3	65	99.1
2	1.3	3	50	69.3
3	1.3	4	65	74.3
4	1.3	4	50	52.4
5	1.3	5	65	59.4
6	1.3	5	50	41.6

3.3.1.2 SLM (high power, high speed)

An experimental matrix was developed using the Taguchi method (Athreya and Venkatesh, 2012) to manufacture the samples. A fibre laser with a large spot size (480 μm) was used to enable high power, coupled with the availability of the fibre. The smaller spot size (250 μm) fibre laser could not achieve the high powers which needed to be evaluated. Table 3.3 shows the matrix used to determine optimum parameters for Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo alloys using high powers and speeds. At the time of conducting these high power, high speed experiments, the β -alloy was still being procured and was therefore not included.

In an attempt to improve the melting of Mo particles, the average Mo particle size was decreased. Hence Ti-6Al-4V had a particle size of 45-100 μm and Mo had a particle size of below 32 μm using a sieve with 32 μm mesh size. To accommodate this change in particle size, the layer thickness was kept constant at 65 μm . The main reason for varying the hatch overlap was also an attempt to increase the melting of Mo by increasing the area of the heat interaction. A greater overlap means that the previous layers are reheated more.

Table 3.3: Experimental matrix for high power, high speed Ti-6Al-4V and Ti-6Al-4V+ 10 wt% Mo samples manufactured with the SLM machine.

Sample ID	Power (kW)	Speed (m/s)	Hatch overlap (%)	Energy density (J/mm^3)
A	2	4	80	80.1
B	2	4	50	32.1
C	2	2	80	160.3
D	2	2	50	64.1
E	3	4	80	120.2
F	3	4	50	48.1
G	3	2	80	240.4
H	3	2	50	96.2

3.3.2 Manufacturing with the LENSTM machine

Similar to the PBF process (SLM machine), manufacturing via the DED process was done under an argon atmosphere using a LENSTM machine (Figure 3.4). The powder was deposited via an injection nozzle system. The heat source (laser) then passed through the centre of the

nozzles and melted the powder onto the base plate according to the CAD design. Instead of the base plate moving down to process the next layer, as in the SLM machine, the nozzle system moved up the same distance as the layer thickness. The process continued until the sample was complete.

3.3.2.1 DED (low power, low speed)

Samples for the LENSTM blown powder system were produced from premixed Ti-6Al-4V+10 wt% Mo powder where the particle size of Ti-6Al-4V was 45-100 μm and the particle size of Mo was between 45-60 μm (Table 3.4). This is because the LENSTM blown powder system works more efficiently with a larger particle size, while the SLM machine can handle a smaller particle size range. Only the β -Ti alloy (Ti-6Al-4V+10 wt% Mo) alloyed *in situ* was duplicated on the LENSTM machine as a means of comparison with the SLM produced *in situ* alloy. The powder set point was kept at 1.7 rpm, and the samples were built in the shape of coupons with two contours and two different hatches, one at 0° and the other at 90°, which were found to give the optimum build parameters and shape (Figure 3.5).

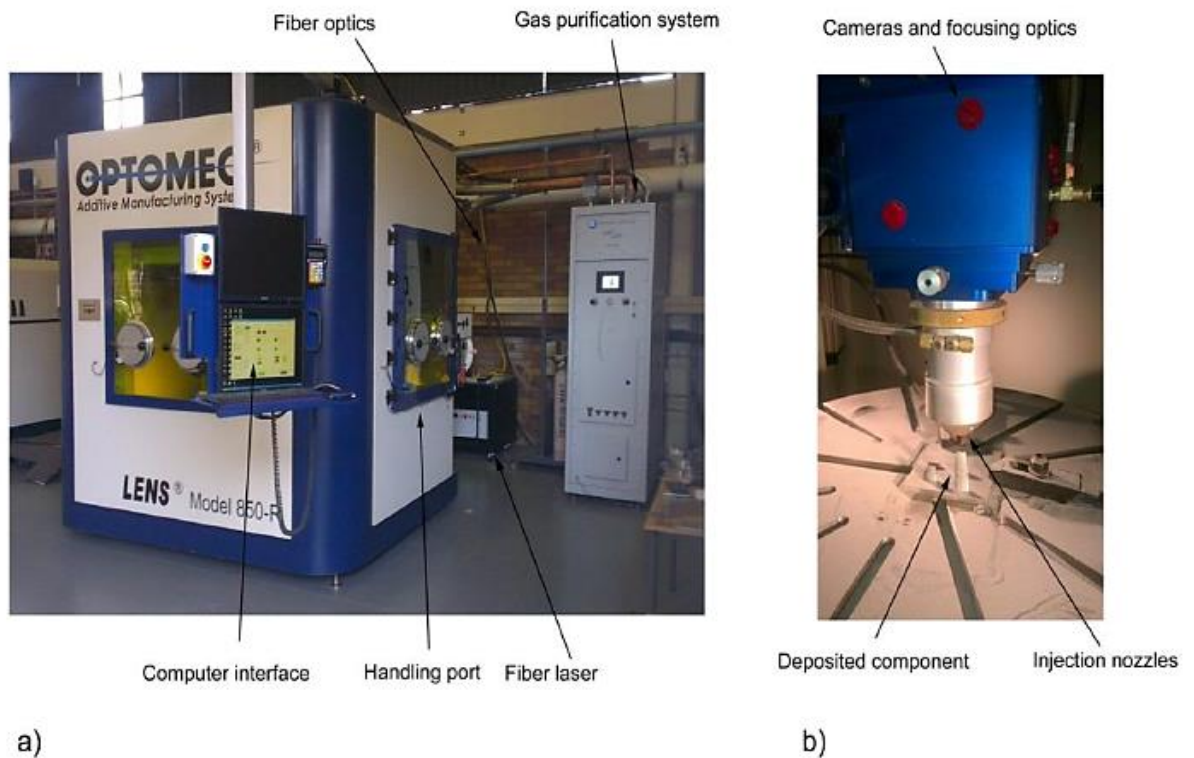


Figure 3.4: Photographs of the LENSTM machine: (a) Full Optomec LENSTM machine set-up, and (b) Injection nozzle and stage.



Figure 3.5: Coupon shaped samples of Ti-6Al-4V+10 wt% Mo built in the LENS[™] machine (the samples are 15 mm across and 11 mm high).

The powers and speeds utilized by the LENS[™] system were considerably lower than those used by the SLM machine. This was expected to give better dissolution of Mo for Ti-6Al-4V+10 wt% Mo alloy and therefore achieve a fully β microstructure as a result of the increased laser-powder interaction time afforded by the LENS[™]. Hence, it was more important to produce the Mo-containing alloy rather than Ti-6Al-4V and Ti-5Mo-5V-2Cr-3Al in the LENS[™] machine, because these commercial alloys do not have the same melting problems (Vrancken *et al.*, 2014).

Table 3.4: Experimental matrix for low power, low speed Ti-6Al-4V+10 wt% Mo samples, manufactured with the LENS[™] machine.

Sample ID	Power (W)	Speed (mm/s)	Hatch overlap (%)	Layer thickness (mm)	Energy density (J/mm ³)
1	360	10.58	50	0.3	202.5
2	360	8.46	50	0.3	253.2
3	400	8.46	50	0.3	281.3
4	400	10.58	50	0.3	225.0

3.4 Sample analysis

Figure 3.6 outlines the sample analysis procedure undertaken for the samples built by PBF and direct energy deposition (DED) processes. The samples were metallographically prepared and porosity measurements were done using Stream Essentials software (identifies percentage of different phases). Optical microscopy was done on each sample and images were taken at the bottom, middle and top of the sample at different magnifications. These optical images, coupled with the porosity measurements were then used to determine the optimum parameters. Scanning electron microscopy and phase analysis via EBSD/ XRD were then conducted on the chosen samples.

Both micro- and macro- Vickers hardness measurements were conducted on the β -Ti alloy alloyed *in situ* produced on both machines, while only micro-Vickers hardness measurements were taken for the commercial alloys. For the DED samples, only porosity and hardness were evaluated because the main focus was on PBF processing, and DED was only done for comparison. The microstructure and hardness results would provide an indication of whether the addition of 10% Mo would increase ductility. Tensile sample manufacturing and testing was then conducted on the commercial β and commercial Ti-6Al-4V alloys to investigate the possibility of the commercial beta alloy being a more suitable material for additive manufacturing compared to Ti-6Al-4V built at the same processing parameters.

Tensile samples were not manufactured for the Ti-6Al-4V+10 wt% Mo composition, because the as-built microstructure was too inhomogeneous, leading to inconsistent hardness results. The micro-galvanic corrosion effects also contributed to this alloy being eliminated as a possible solution to the problem. Therefore it was decided that no further investigations would be done on it. Micro-galvanic corrosion effects with the as-built β -Ti alloy alloyed *in situ* produced via the PBF process was a concern, due to the poor melting of the Mo particles, therefore a sample built at the highest speed with the highest fraction of unmelted particles was immersed in a 3.5% NaCl solution over 20 weeks to observe the effects of corrosion.

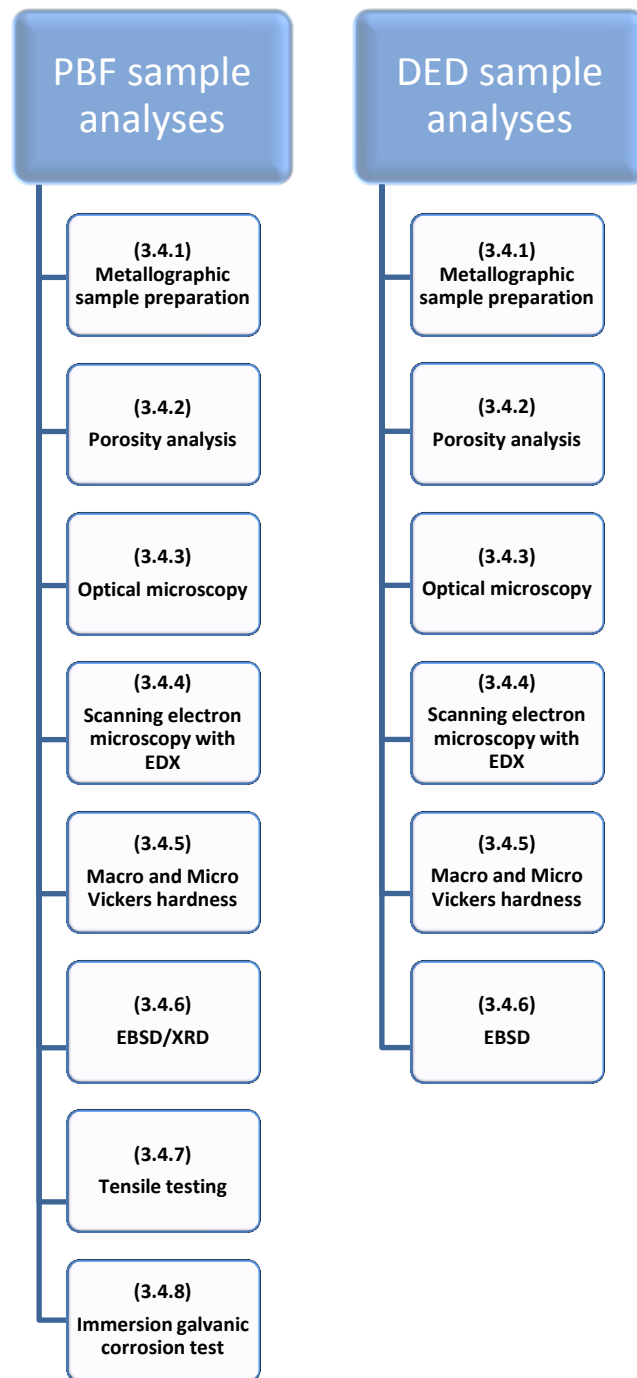


Figure 3.6: Summary of experiments conducted on the samples produced via the PBF (SLM) and DED (LENSTM) processes.

3.4.1 Metallographic sample preparation (Both SLM and DED samples)

3.4.1.1 Cutting

Cutting was done to obtain a more manageable sample to analyse with microscopy and for hardness testing. Samples were cut using a Struers Discom -2 cut off machine. This is an

abrasive cutting machine that uses rotating disks which were mainly made up of abrasive particles bonded by a suitable medium. The consumable disk used for cutting all samples was a Corundum F-type disk which is specifically used for materials like titanium alloys. In abrasive cutting, a coolant is usually used to prevent mechanical and thermal damage and in this case, water was used.

3.4.1.2 Mounting

Mounting, in conjunction with cutting, was important to do for handling of small samples during examination. Mounting was done on both a Struers Presto mounting press-2 machine and on a AMP 50 automatic press machine, using conductive resin. Careful monitoring of the pressure was needed on the Struers Presto machine, because a drop in pressure during the heating stage would lead to cracking of the resin.

3.4.1.3 Grinding

Grinding was done on a Struers Tegrapol-25 grinding and polishing machine. The samples were first ground with silicon carbide 320 grit paper. The grit paper was changed to 1200 for finer grinding. The final grinding stage was done using 4000 grit paper and after this stage no visible scratches were seen on the samples.

3.4.1.4 Polishing

To obtain a mirror finish, a MD-CHEM polishing cloth was used with colloidal silica 50nm/OP-S 0.04µm as lubricant.

3.4.2 Porosity analysis

Porosity analyses on the SLM and DED samples were done on the etched cross-sectioned samples. The cross-sections were analysed using image analysis (Stream essentials) software on images taken at 50x, the pores were determined at a magnification of 50x. For analysis the pores and the sample microstructure were identified as two different phases.

3.4.3 Optical microscopy

Optical microscopy was done with an Olympus BX51M microscope for all the samples. The areas of focus analysed were the bottom, middle and top. Images were taken at 50x, 100x and 200x magnifications.

3.4.4 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy

Scanning electron microscopy (SEM) in backscatter and secondary electron modes was done to further analyse the microstructures. The images were taken at low magnifications (43x) to

obtain an overview of the sample surface. The magnification was increased to 100x and then at higher magnifications of 1000x and 3000x. Energy dispersive X-ray spectroscopy (EDX) was done to investigate the elemental composition of different areas.

3.4.5 Macro and Micro Vickers hardness

Micro-Vickers hardness measurements were done on samples which were produced from optimum parameters. The tests were done on a Zwick Roell ZHV μ Vickers hardness machine by applying a load of 300 g for a dwell time of 10 seconds. A hardness profile was taken from the bottom (closer to build platform) of each sample to the top (at maximum height). Macro-Vickers hardness measurements were done on a Future-Tech FV-700 Vickers hardness machine by applying a load of 20 kg for a dwell time of 10 seconds. The macro-Vickers hardness tests were only conducted on Ti-6Al-4V+10 wt% Mo sample with optimized parameters, produced with the SLM machine and the LENSTM machine for comparison.

3.4.6 Electron Backscatter Diffraction and X-Ray Diffraction

For the Ti-6Al-4V+10 wt% Mo samples produced with the SLM machine (low power and high speed), X-ray diffraction (XRD) was done using a Panalytical X'pert PRO PW3040/60 X-ray diffractometer with a Cu K α ($\lambda = 0.154$ nm) monochromated radiation source. XRD was used to identify the phases present in the *in situ* manufactured alloy. After the phases were confirmed, Electron Backscatter Diffraction (EBSD) was then conducted on the samples that followed to identify the location of each phase in the microstructure of the sample.

3.4.7 Tensile testing

Tensile samples were machined into a 'dog bone' shape (Figure 3.7) and tensile tests were done using the ASTM E8 M standard (ASTM International, 2009) at the CSIR Material Testing Laboratory. Tensile testing was only done for Ti-6Al-4V and the β -Ti alloy and only three samples were made for each alloy.

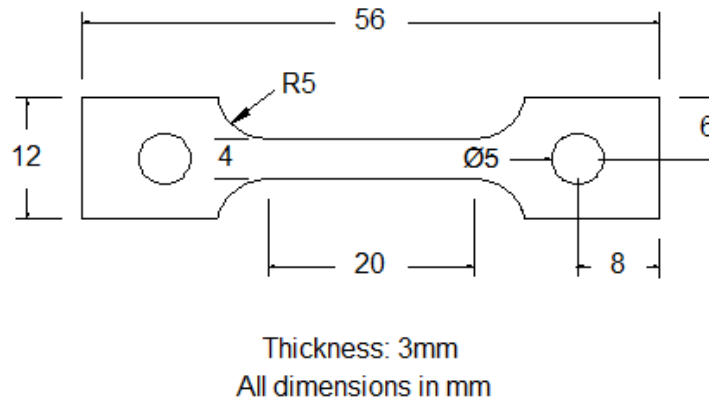


Figure 3.7: Schematic diagram of tensile samples.

3.4.8 Micro-galvanic corrosion experiments

The micro-galvanic effects between unmelted Mo particles and Ti-6Al-4V were considered as a possible problem, therefore further investigations were done. A β alloy sample (Ti-6Al-4V+10 wt% Mo) alloyed *in situ* produced on the SLM machine at the highest speed was chosen for this experiment because it had the highest fraction of unmelted Mo particles. To make a 3.5% NaCl solution, 108.8 g of sodium chloride was dissolved in 3000 ml of distilled water in a 5-litre plastic bucket. An area of focus in the form of a circle was drawn on the surface of a polished sample using Vickers indentations. The sample was tied with non-conductive thread and the other end of the thread was tied to a stick which was placed on the top of the bucket. The polished sample was then submerged in the prepared solution. The experiment was left in the solution for a week, accompanied by stirring of the solution twice a day in order to make sure there was sufficient oxygen for possible corrosion reactions. The solution was also replenished biweekly to compensate for evaporation. Optical microscopy was done on the samples before the experiment and after each week for 20 weeks. SEM with EDX was also done for closer examination.

Chapter 4: Results

4.1 Powder Characterization

Before the manufacturing of the samples, powder characterization was conducted to verify that the powder specifications given by the supplier was correct. In the case where powder mixing took place, the verification that proper mixing took place was important.

4.1.1 Characterization of Ti-6Al-4V+10 wt% Mo powder

Figure 4.1 (a) shows that the morphology of both Ti-6Al-4V (dark particles) and the Mo (light particles) were spherical. However, some of the Ti-6Al-4V particles showed some visible porosity. At a magnification of 200x, only two particles appeared to have pores out of the whole sample. The porosity arises from the air trapped in the molten metal, which remains as gas bubbles. This material porosity was undesirable as it would add to the process/manufacturing porosity, thereby decreasing the build quality of the finished samples.

Figure 4.1 (b) shows the particle size distribution curves of the Ti-6Al-4V (red curve) and Mo (blue curve) mixed powder. Most of the Mo particles had sizes between 20-60 μm with the d_{50} at 38 μm . The Ti-6Al-4V particles were larger than the Mo particles, with a size range of 50-100 μm and the d_{50} at 76 μm .

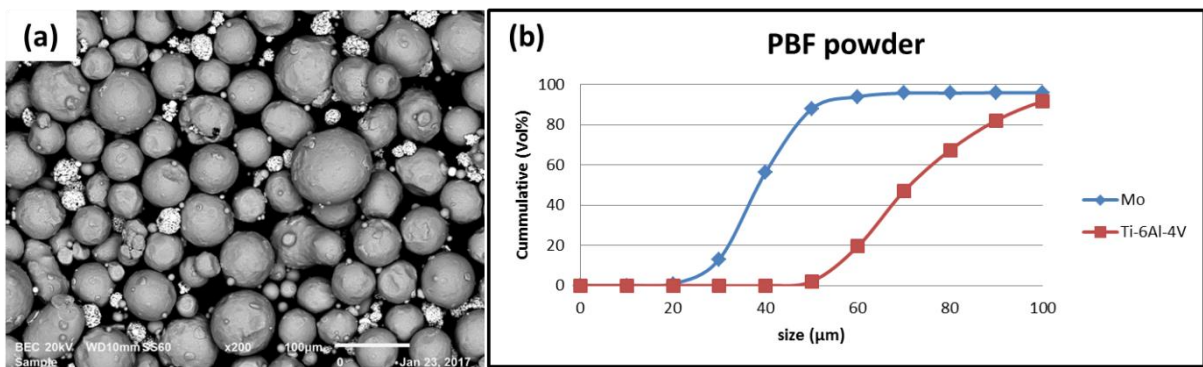


Figure 4.1: PBF powder characterization: (a) SEM-BSE image showing powder morphology, (b) Powder particle size distribution curves.

Molybdenum powder with different particle sizes was used for the direct energy deposition (DED) process although the mixing procedure was identical to that done for the Powder Bed

Fusion (PBF) powder. Figure 4.2 (a) shows that the morphology of the Ti-6Al-4V (dark particles) and the Mo (light particles) was also spherical.

Figure 4.2 (b) shows the particle size distribution curves of the Ti-6Al-4V (red curve) and Mo (blue curve) mixture. As stated in Section 3.3.2.1, as per the requirements of the LENSTM machine, the powder particles had to be between 45-100 μm for good powder flowability. Therefore, both the Ti-6Al-4V and Mo powders had a similar particle size range as opposed to the PBF powder. The Ti-6Al-4V powder had particle sizes ranging from 50-100 μm with d_{50} at 77 μm , while the Mo powder particle sizes ranged from 50- 90 μm with d_{50} at 60 μm .

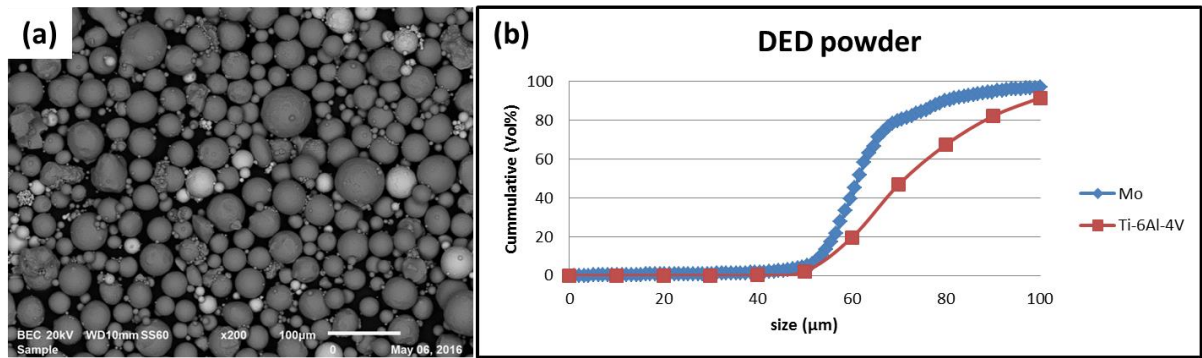


Figure 4.2: DED powder characterization: (a) SEM-BSE image showing powder morphology, (b) Powder particle size distribution curves.

4.1.2 Characterization of β -Ti alloy powder

Figure 4.3 (a) shows that the morphology of the β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) particles was spherical for most of the particles with some irregularly shaped particles sparingly present. Figure 4.3 (b) shows the particle size distribution curve for the β -Ti alloy, which indicates that particles ranged from 20-100 μm with d_{50} at 70 μm .

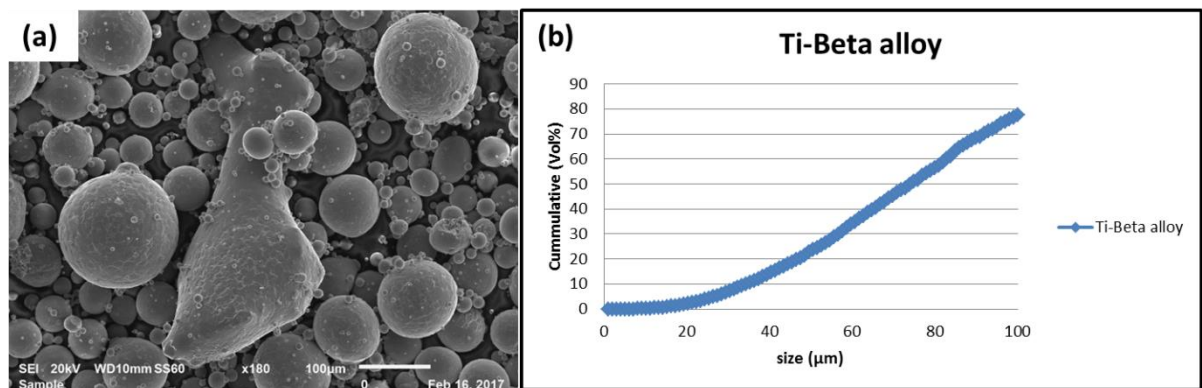


Figure 4.3: β -Ti alloy powder characterization: (a) SEM-SEI image showing powder morphology, (b) Powder particle size distribution curve.

4.2 Parametric study

The effect of the different process parameters had to be understood, especially when trying to find the correct combination to give the least porosity (due to lack of fusion or gas bubbles between particles) and other sample defects, such as unmelted powder particles.

Figure 4.4 shows optical images for Ti-6Al-4V samples produced at different processing parameters. Images were taken at the bottom, middle and top and are sorted from the lowest energy density to the highest energy density. As the energy density increased, the build quality increased and the porosity decreased. At lower energy densities the columnar prior β grains were thinner than those seen at higher energy densities.

4.2.1 Effect of energy density on the build quality (Ti-6Al-4V)

The build quality refers to a combination of factors that were inspected during and after the manufacturing of the samples. These factors were in the form of questions that needed to be answered upon visual inspection of the sample, such as:

1. Did the sample delaminate from the base plate during manufacturing?
2. Did the manufacturing of the sample stop due to spatter or uneven building?
3. Was there severe lack of fusion between layers? The lack of fusion was evaluated by ascertaining whether two or more layers did not adhere to each other.

If the answer was yes to any of these questions then the response would be '0', but if the answer was no for all three questions then the response would be '1'.

Figure 4.5 shows that only three of the six samples that were built received a response of one. Using energy densities lower than 64.1 J/mm^3 did not give the desired build quality, while using energy densities between $80\text{-}160 \text{ J/mm}^3$ yielded an acceptable build quality. Utilizing an energy density greater than 160 J/mm^3 produced too much heat, so that the sample could not be built and hence the process had to be aborted.

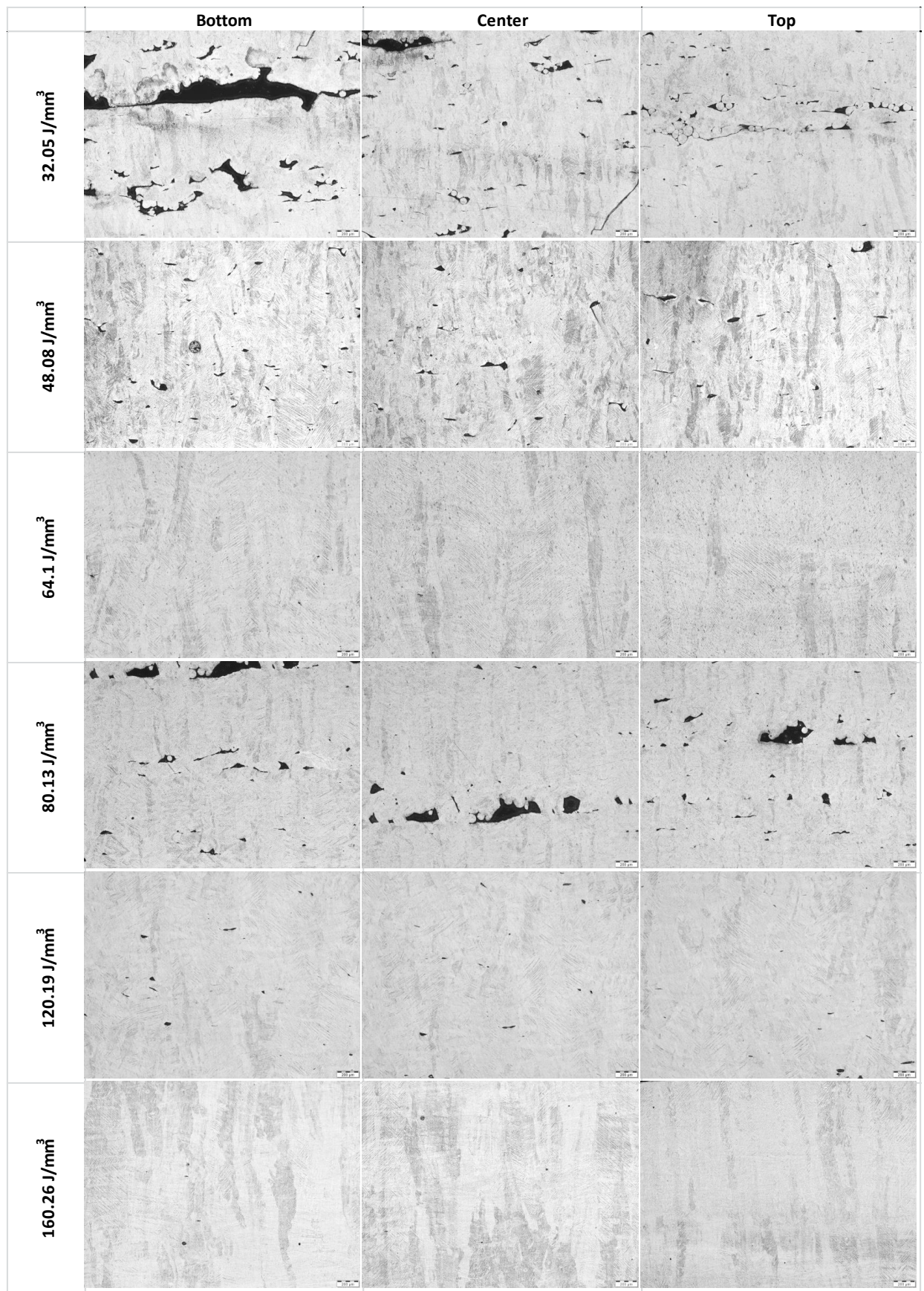


Figure 4.4: Optical micrographs (scale bar: 200 μ m) showing the effect of energy density on the build quality for Ti-6Al-4V built on the SLM machine.

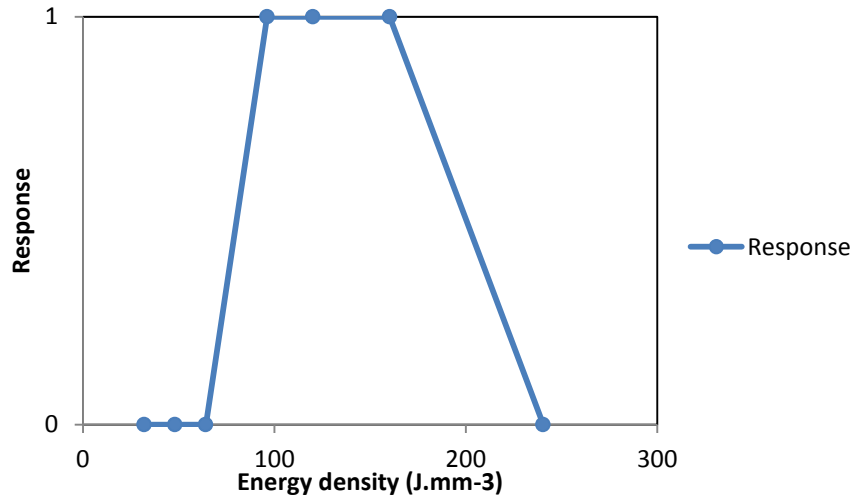


Figure 4.5: Effect of energy density on the build quality for Ti-6Al-4V built on the SLM machine.

4.2.2 Effect of energy density on sample porosity (Ti-6Al-4V)

To determine the relationship between the energy density and the porosity, two samples which passed the response test and two samples which failed the test were used. Figure 4.6 shows that an exponential relationship exists between the energy density and the porosity for the Ti-6Al-4V samples built on the SLM machine according to Equation 4.1. The R^2 value was fairly high (0.9714) meaning that the exponential model fits the data well. As the energy density increased, the porosity decreased exponentially.

$$y = 6.0566e^{-0.028x}$$

Equation 4.1

4.2.3 Effect of energy density on sample porosity (β -Ti alloy)

Due to the fact that there was no previous work done in additive manufacturing for this specific β -Ti alloy (Ti-5Mo-5V-2Cr-3Al), the safest option during processing was to start with base parameters currently proven to work for Ti-6Al-4V at the CSIR. Figure 4.7 shows the resultant optical images of samples that were built using these parameters. As observed for Ti-6Al-4V, as energy density increased, the build quality increased and the porosity decreased.

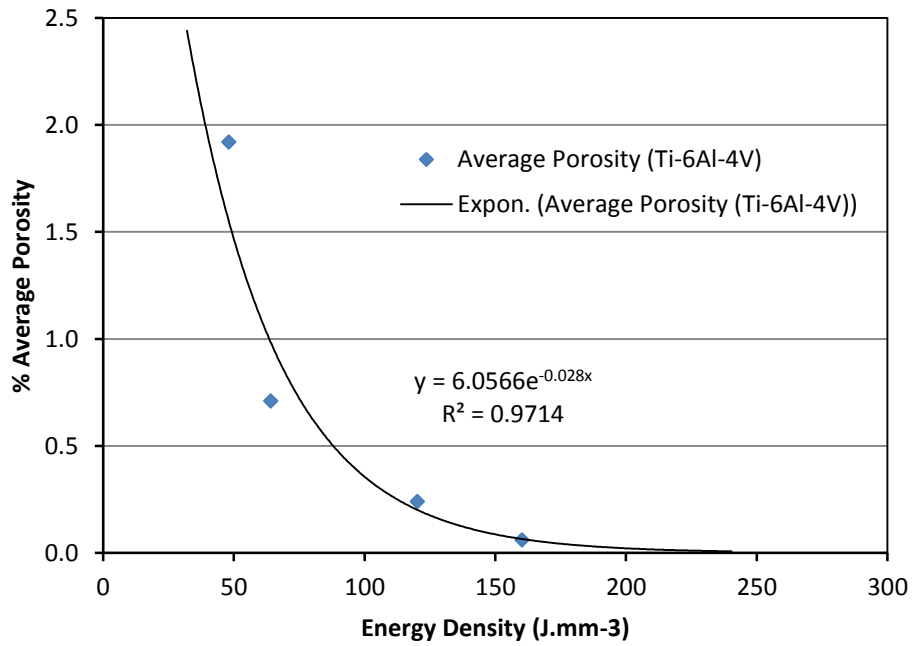


Figure 4.6: Graph showing the effect of energy density on sample porosity for Ti-6Al-4V samples built on the SLM machine.

Wave-like structures separating each layer were seen perpendicular to the build direction. There were also columnar β grains growing in the build direction. There was no sign of unmelted particles in the microstructure, but there seemed to be sites where finer material fused together to form dark areas, which could be mistaken as porosity at lower magnifications (50x). The porosity measurements were taken with careful consideration of these sites for better accuracy.

Figure 4.8 shows a curve indicating the relationship between the energy density and the porosity of the β -Ti alloy. The curve shows that a polynomial relationship exists between the energy density and the porosity for the β -Ti alloy samples built on the SLM machine according to Equation 4.2. The R^2 value (0.8976) shows that the polynomial model was a fair fit for this data. However, an exponential decay relationship may better fit the data at high energy density values.

$$y = 0.0027x^2 - 0.4756x + 20.967$$

Equation 4.2

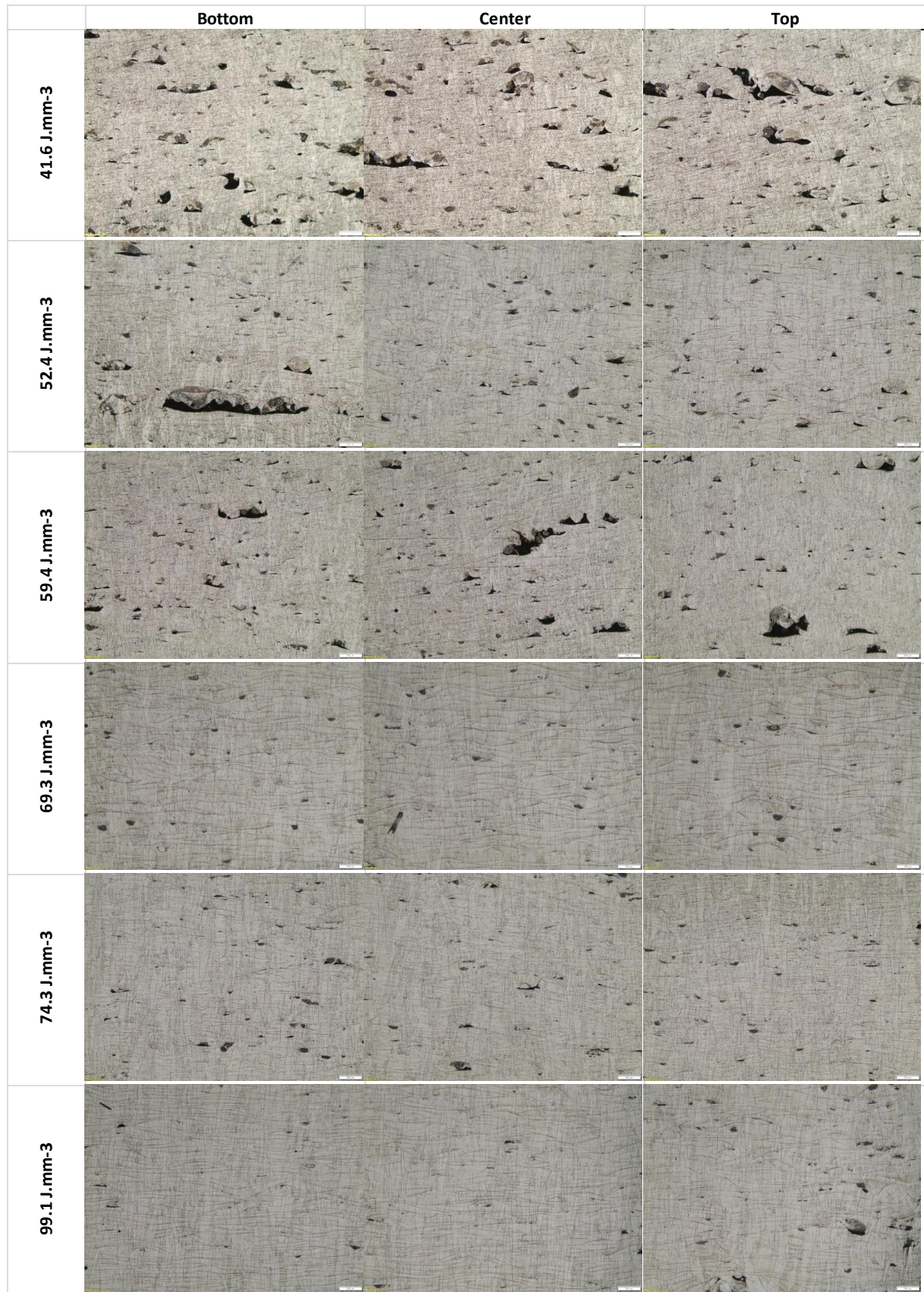


Figure 4.7: Optical micrographs (scale bar: 200 μm) showing the effect of energy density on the build quality for β -Ti alloy built on SLM machine.

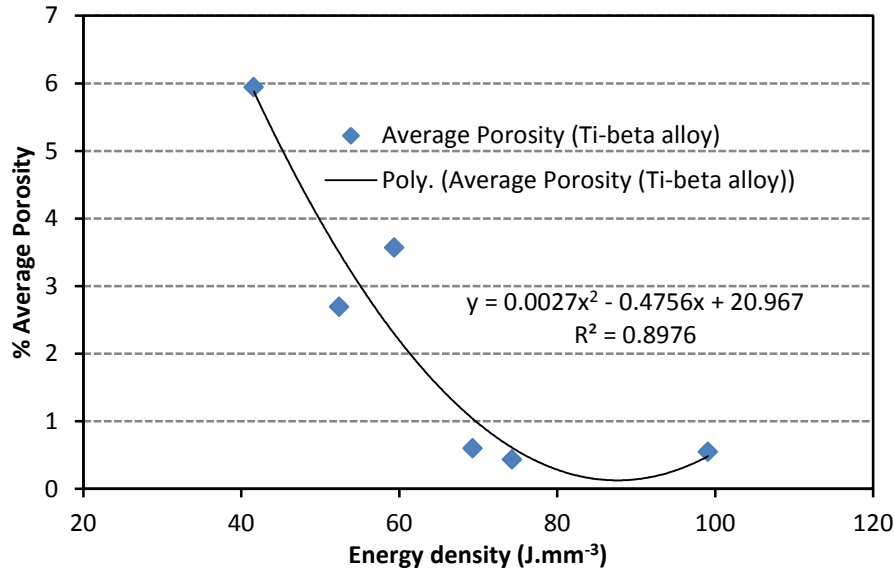


Figure 4.8: Effect of energy density on sample porosity of β -Ti alloy.

4.2.4 Effect of the addition of Mo to Ti-6Al-4V (*in-situ* alloyed powders)

The addition of Mo to Ti-6Al-4V greatly changed the microstructure of the alloy. Figure 4.9 shows a similar trend to that seen in Ti-6Al-4V (Figure 4.4) and the β -Ti (Figure 4.7) alloy: as the energy density increased, the build quality increased and the porosity decreased. The wave-like structure separating the different layers observed in Figure 4.7 for the β -Ti alloy, was more prominent in the β -Ti alloyed *in situ*. The different contrasts (light and dark areas) of some layers were also visible on the micrographs, indicating signs of inhomogeneity in terms of dissolved Mo.

4.2.4.1 Effect of energy density on the build quality

Figure 4.10 shows the effect of the energy density on the build quality. The only energy densities which resulted in unacceptable build qualities were at the lowest (32.051 J/mm³) and the highest (240.385 J/mm³) tested values. Comparing Figure 4.5 (Ti-6Al-4V with no Mo) with Figure 4.10 (Ti-6Al-4V with Mo), it was evident that the addition of Mo improved the build quality at energy densities where the Ti-6Al-4V had failed.

4.2.4.2 Effect of energy density on sample porosity

Figure 4.11 shows the relationship between the energy density and sample porosity. The curve shows that a polynomial relationship exists between the energy density and the porosity of Ti-6Al-4V+10 wt% Mo alloyed *in situ* produced on the SLM machine according to Equation 4.3. The R^2 value 0.9514 indicates a reasonable fit.

$$y = -4 \times 10^{-5}x^2 + 0.0052x + 0.3737$$

Equation 4.3

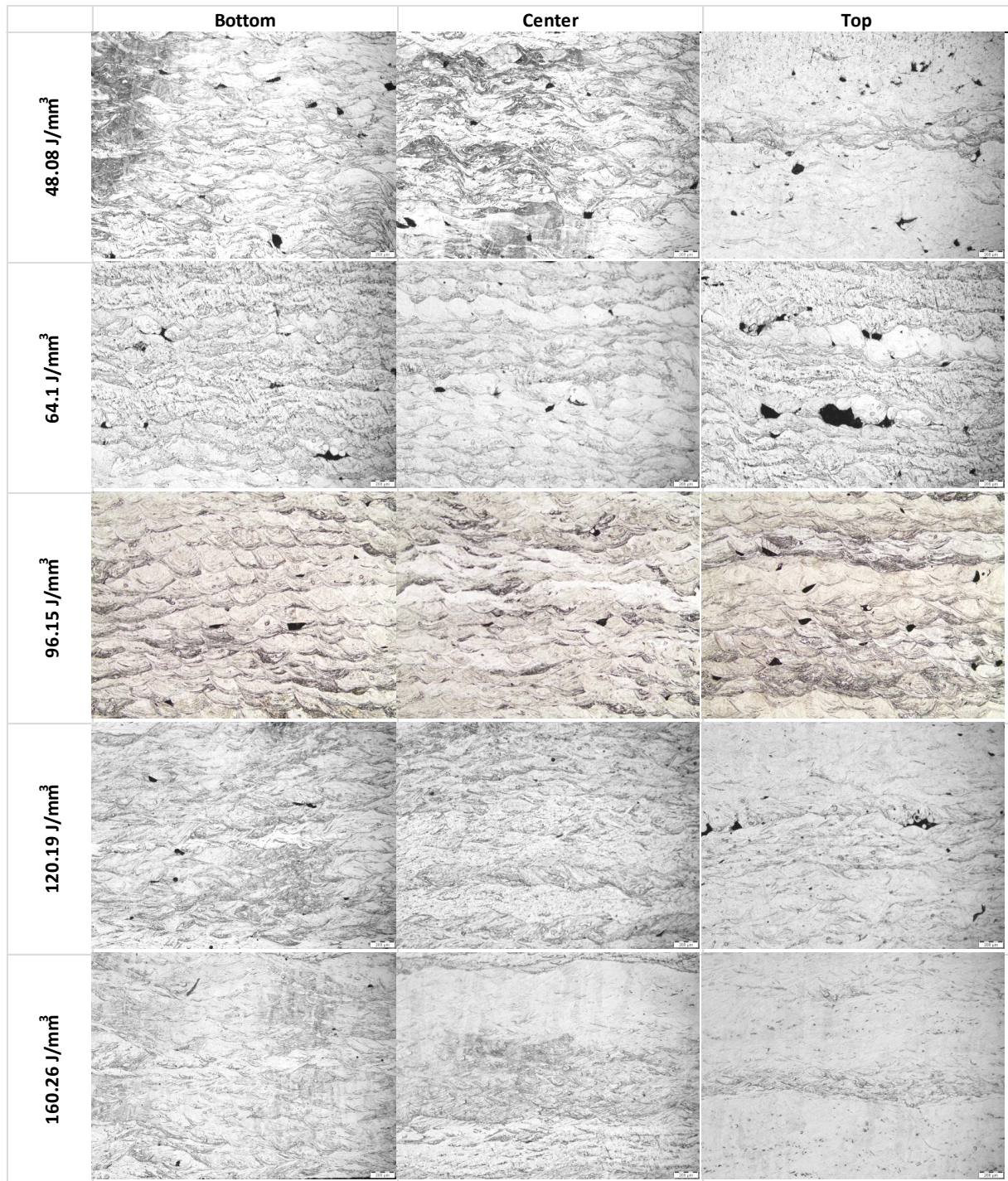


Figure 4.9: Optical micrographs (scale bar: 200 μ m) showing the effect of energy density on the build quality for Ti-6Al-4V+10 wt% Mo built on the SLM machine.

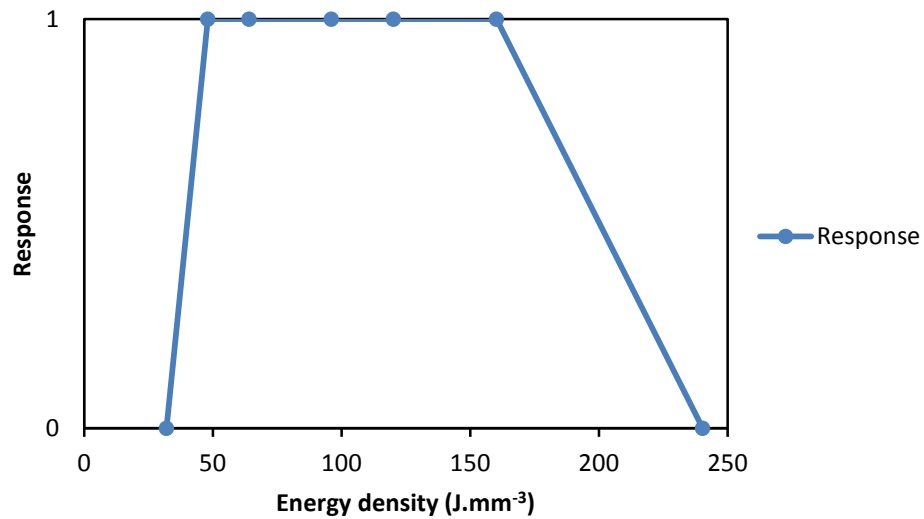


Figure 4.10: Effect of energy density on the build quality for Ti-6Al-4V+10 wt% Mo.

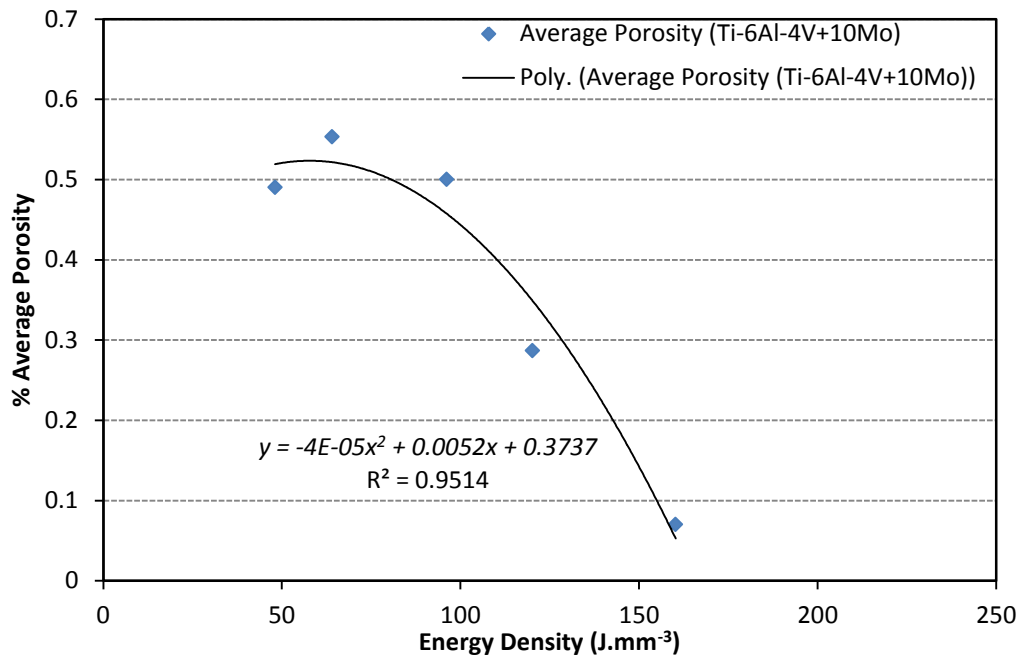


Figure 4.11: Effect of energy density on sample porosity of Ti-6Al-4V+10 wt% Mo built on the SLM machine.

4.2.4.3 Effect of speed on the dissolution of Mo

As a result of the large difference in the liquidus temperature of Ti-6Al-4V (1660°C) and the melting point of Mo (2623°C), the processing speed was an important parameter in obtaining complete dissolution of Mo.

Figure 4.12 shows the micrographs of Ti-6Al-4V+10 wt% Mo alloyed *in situ*. The micrographs show no apparent difference in the amount of undissolved Mo, but after analysis

with the Stream Essentials software which calculated the percentage of each phase, it was evident that as speed increased, the dissolution of Mo decreased.

Figure 4.13 shows the relationship between speed and proportion of undissolved Mo particles. As the speed increased, the number of undissolved Mo particles increased. There were five times more unmelted particles found at the highest speed of 4 m/s (Figure 4.12a) than those found at the lowest speed of 2.5 m/s (Figure 4.12d). No significant difference in dissolution was observed between the samples that were processed at 3 m/s and at 3.5 m/s.

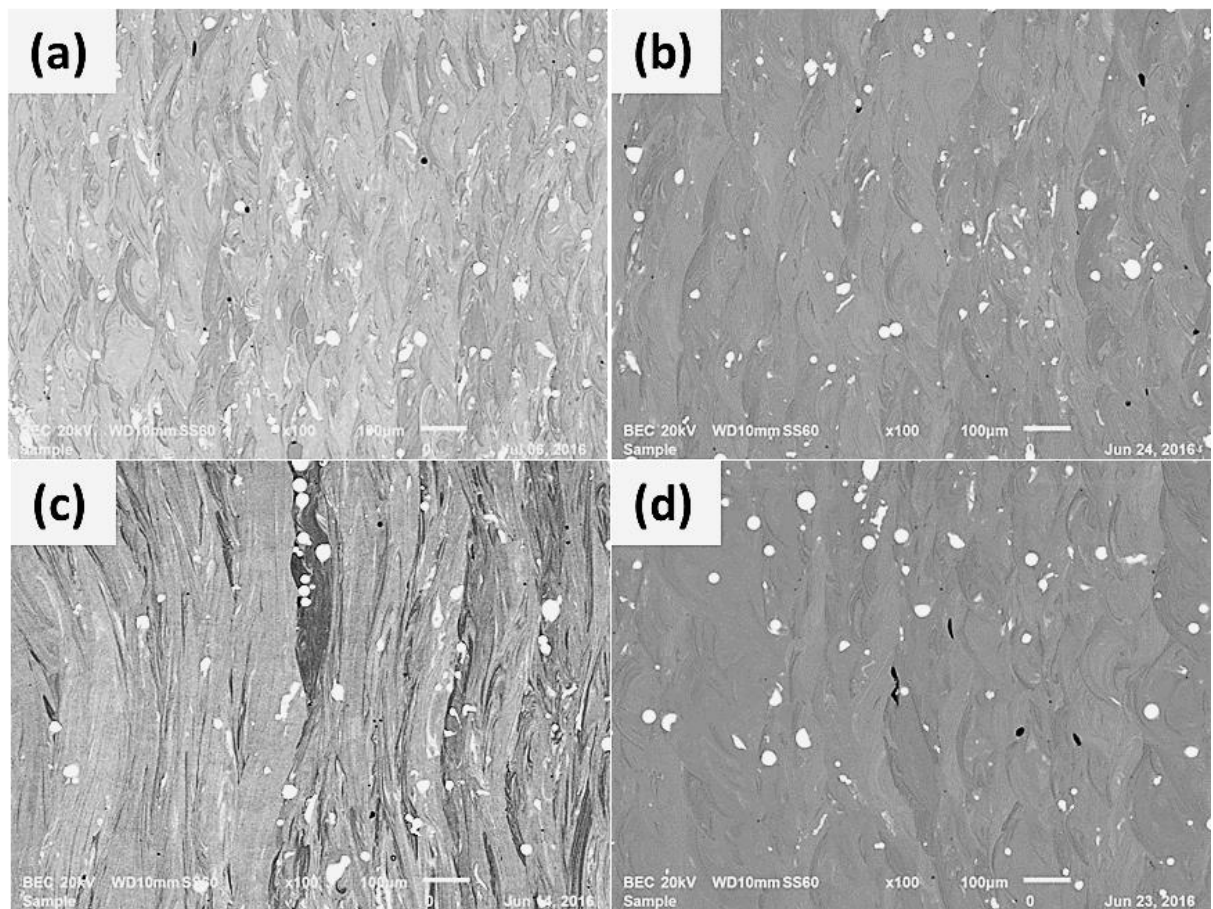


Figure 4.12: SEM-BSE images showing the effect of speed on the dissolution of Mo (white particles) where the build direction was from left to right built at a speed of: (a) 4 m/s, (b) 3.5 m/s, (c) 3 m/s and (d) 2.5 m/s

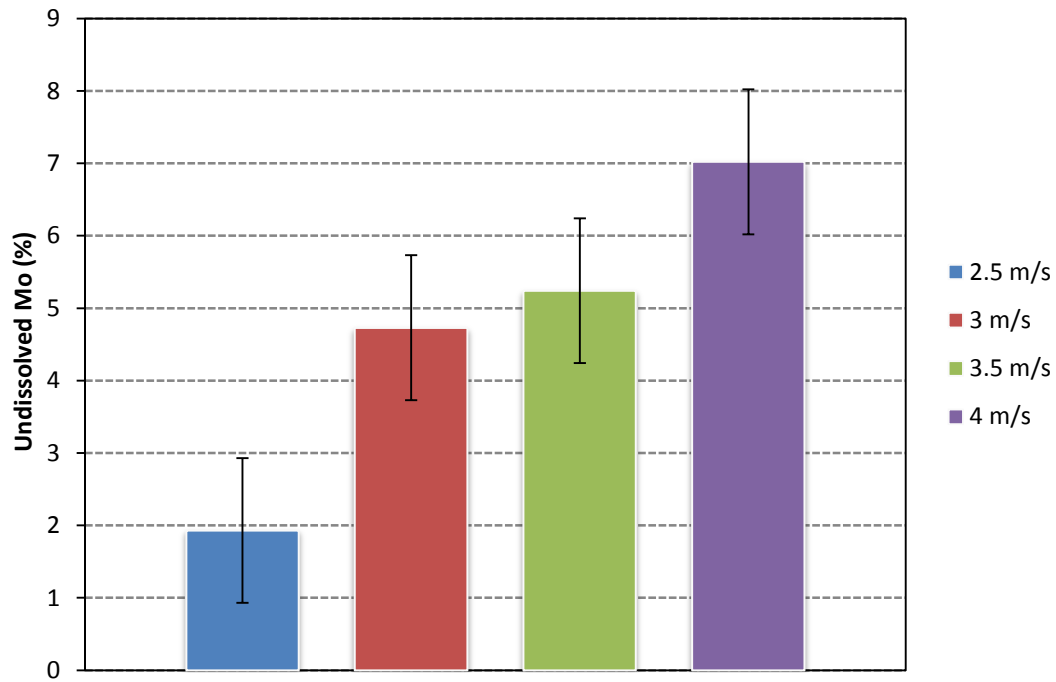


Figure 4.13: Effect of speed on the dissolution of Mo in Ti-6Al-4V.

4.2.4.4 Effect of hatch overlap on the dissolution of Mo

The hatch overlap (the percentage one track overlaps another) was identified as another important parameter with regards to the dissolution of Mo. The increase in hatch overlap was expected to improve the heating, and therefore also improve the dissolution of Mo.

Figure 4.14 shows graphs demonstrating the relationship between the hatch overlap and undissolved Mo particles. At the highest power (3 kW) and the highest speed (4 m/s), increasing the hatch spacing had no significant influence on the dissolution of Mo (Figure 4.14a). At the lowest power (2 kW) and at the lowest speed (2 m/s), increasing the hatch overlap greatly improved the dissolution of Mo, by reducing the remaining unmelted particles from 5.8% to 0.7% (Figure 4.14b).

There was a large margin of error in these results due to the inhomogeneity of the microstructure. There were some areas that had a much larger concentration of undissolved Mo particles, and areas where there was a negligible amount of undissolved Mo, but this was a random distribution. The combination of low power and low speed coupled with the larger hatch spacing was more beneficial to the improvement of the dissolution of Mo than the combination of high power and high speed coupled with the larger hatch spacing.

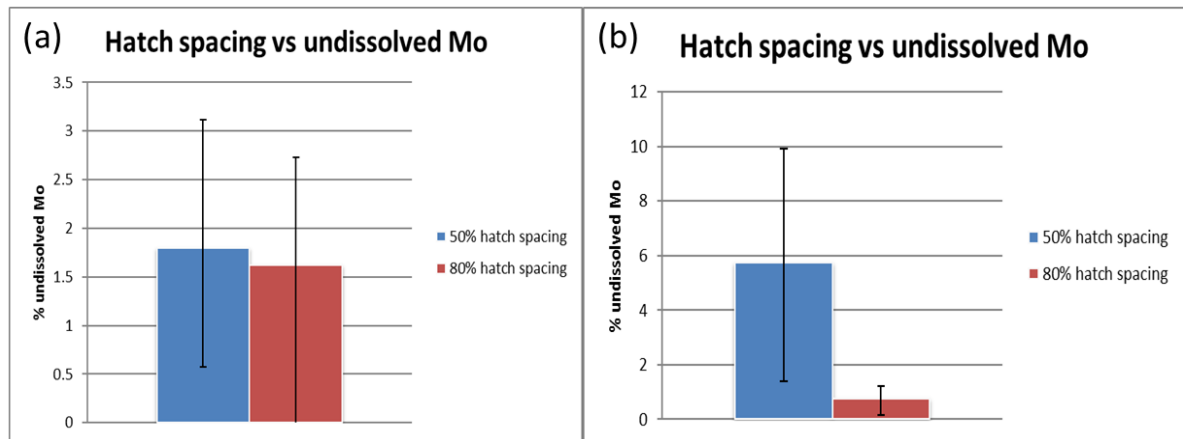


Figure 4.14: Effect of hatch overlap on the dissolution of Mo in Ti-6Al-4V+10 wt% Mo built on the SLM machine at: (a) 3 kW and 4 m/s and (b) 2 kW and 2 m/s.

4.2.4.5 Effect of power on the dissolution of Mo

Lastly, power is another parameter which greatly influenced the dissolution of molybdenum, as shown in Figure 4.15. As the power was increased, the dissolution of Mo increased. It is important to note that these measurements were taken at the lowest speed of 2 m/s. If the measurements had been taken at the highest speed (4 m/s), there would not be enough time to melt the Mo powder, therefore decreasing the likelihood of any improvement in Mo dissolution.

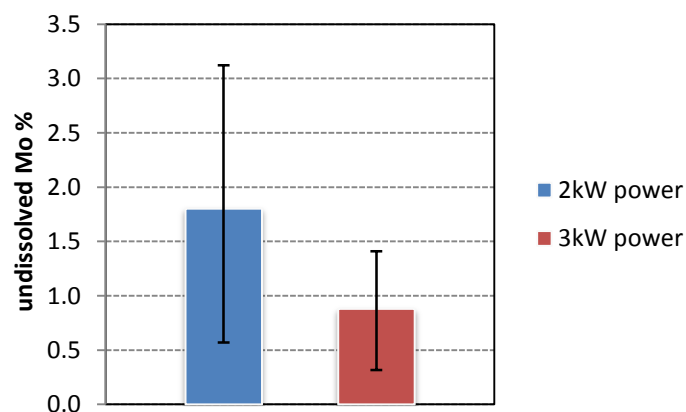


Figure 4.15: Effect of power on the dissolution of Mo in Ti-6Al-4V+10 wt% Mo built on the SLM machine at 2 m/s.

The process parameters had a large influence on the integrity of the built samples. For all samples, the increase in energy density led to an increase in the build quality and a decrease in the porosity. The addition of Mo to Ti-6Al-4V proved to be beneficial, as some of the

parameters which failed the response test using conventional Ti-6Al-4V, passed the test when Mo was added. On studying the influence of the key influential process parameters on the dissolution of Mo, such as speed, hatch overlap and power, it was found that these parameters greatly improved the dissolution of Mo in the following ways:

1. Decreased speed led to decreased amounts of undissolved Mo.
2. Increased hatch overlap led to decreased amounts of undissolved Mo. The improvement was more significant with the combination of low power and low speed, compared to high power and high speed.
3. Increased power led to decreased amounts of undissolved Mo.

As much as these parameters influence the dissolution of Mo, obtaining the correct combination of parameters greatly influenced the results. The parameters that gave the least amount of porosity and the best build quality for both Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo were 2 kW, 2 m/s and at 80% hatch overlap. There was also the least amount of undissolved Mo at these parameters. For the β -Ti alloy, considering the build quality and the porosity, the best parameters were at 1.3 kW, 3 m/s and 50% hatch overlap.

4.3 Study of the microstructure and phase analysis for chosen parameters

4.3.1 Low power & high speed samples

4.3.1.1 Microstructure

For the first set of samples alloyed *in situ* at 1.3 kW, 2.5 m/s and 50% hatch overlap, the microstructure was analysed using a SEM and the phase analysis was done using XRD. These initial tests were done to see if alloying *in situ* could be done on the SLM machine and whether a fully beta microstructure could be obtained. Figure 4.16 shows the microstructure obtained by *in situ* alloying Ti-6Al-4V with Mo with the SLM machine. The microstructure was characterized by wave-like patterns separating each layer (Figure 4.16a) as described in Section 4.2.4. There were also unmelted Mo particles (light particles) visible in the matrix under backscattered electron mode (Figure 4.16b).

Light and dark areas in the matrix of the alloy indicated a difference in composition. Further investigation by X-ray mapping in an area showing such variation (Figure 4.17a) showed a difference in molybdenum content (Figure 4.17b). This indicates that there were areas in the microstructure where more of Mo had dissolved than in other areas, and this was observed in

the polished samples. The areas that were identified as weak points for depleted dissolution were those that looked like grooves or crevices in the microstructure. From EDX analysis, it was then established that even in the areas where Mo had dissolved, the amount was not consistent throughout the matrix. Some areas contained only 4 wt% Mo while other areas contained 9 wt% Mo.

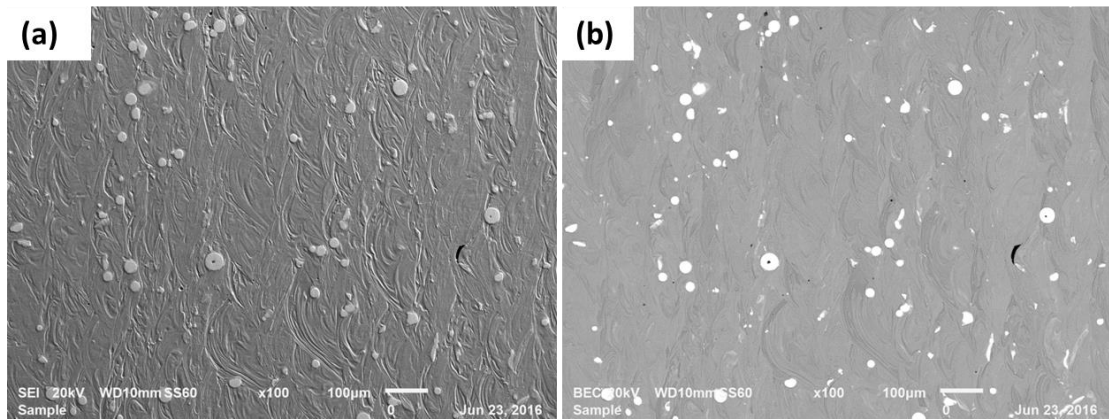


Figure 4.16: SEM micrographs of Ti-6Al-4V+10 wt% Mo made with the SLM machine where the build direction is from left to right built at 1.3 kW power, 2.5 m/s speed and 50 % hatch overlap: (a) SEI mode and (b) BSE mode.

Figure 4.18 shows the XRD results for Ti-6Al-4V+10 wt% Mo built with the SLM machine. Figure 4.18a shows the results of a sample built at the highest speed of 4 m/s. As expected from the microstructural analysis, the sample was not fully β . Both α and β peaks were detected, as well as Mo peaks as a result of unmelted Mo particles. Although the same phases were present in the sample built at the lowest speed of 2.5 m/s (Figure 4.18b), the quantity (number of peaks visible) of the identified α peaks had decreased.

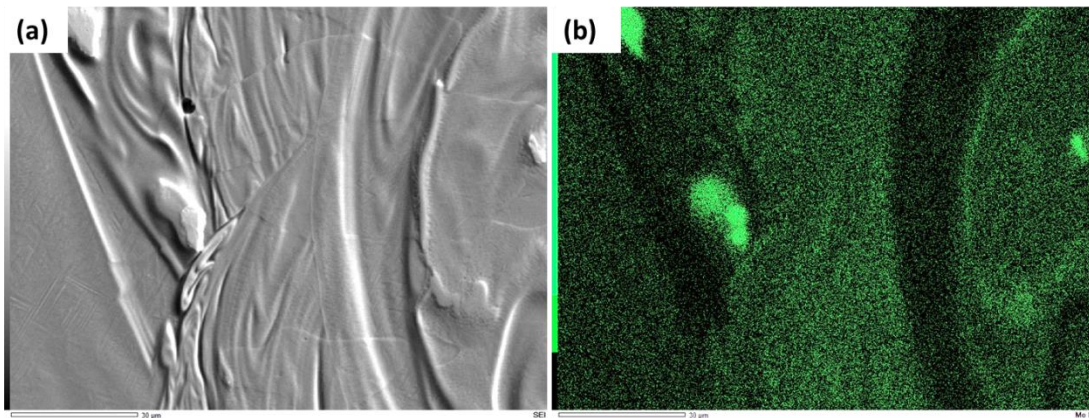


Figure 4.17: SEM-SE micrograph of Mo map done on an area in the microstructure: (a) area of analysis and (b) Mo map.

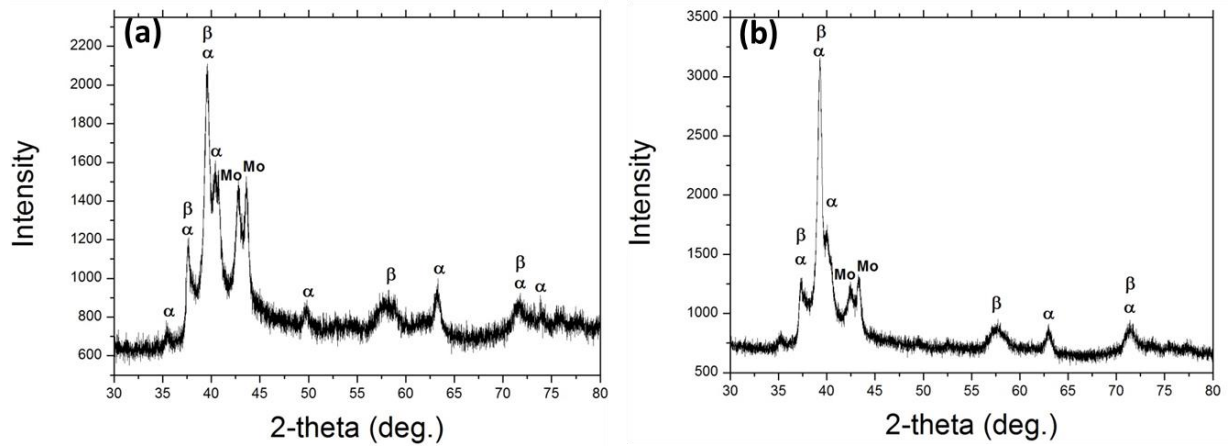


Figure 4.18: XRD results: (a) sample built at the highest speed (4 m/s), and (b) sample built at the lowest speed (2.5 m/s).

4.3.1.2 Micro-galvanic corrosion

After observing the microstructure of Ti-6Al-4V+10 wt% Mo alloyed *in situ*, the micro-galvanic corrosion effects of such an inhomogeneous microstructure became of interest. The sample built at the highest speed, which had the most unmelted Mo particles, was immersed in a 3.5% NaCl solution for 20 weeks, and was analysed weekly.

Figure 4.19 shows the grain structure of a molybdenum particle in the alloy. Figure 4.19a shows the whole un-etched particle while 4.19b shows the particle etched with a solution of 10 ml glycerol, 10 ml HNO₃ and 10 ml HF. The microstructure consisted of grains of different sizes. There were visible smaller grains (sub-grains) inside some grains. There was also porosity which was mostly visible on the grain boundaries, rather than inside the grain.

Figure 4.20 shows the progression of the micro-galvanic corrosion from week 1 to week 20. Comparing Figures 4.19a and 4.20a, significant changes are evident as the particle had visible grain boundaries after a week due to the corrosive attack. There was also a darker contrast area in Figure 4.20a which shows that in that area the corrosion was more severe than other areas. After 20 weeks (Figure 4.20b), it was observed that the particle was separating from the matrix and the prior grain boundaries were more pronounced and deeper.

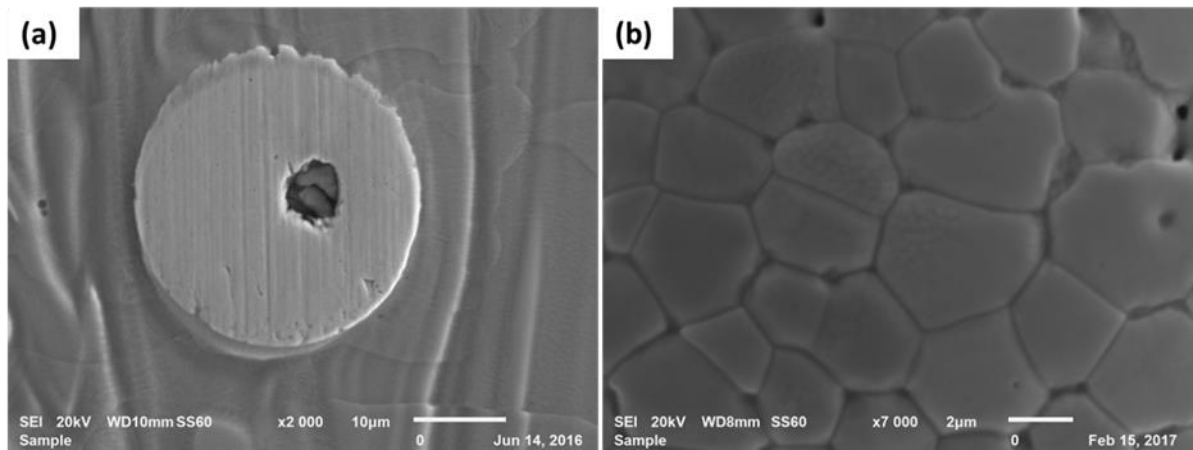


Figure 4.19: SEM-SE images showing grain structure of Mo: (a) Un-etched Mo particle, and (b) etched Mo particle.

Smaller particles (1, 2 and 3) in Figure 4.20(c and d) had corroded to the extent that they had fully detached from the matrix. The degradation of the larger particles (4 and 5) occurred due to detachment of grains/subgrains within the Mo-particles. This was followed by corrosive attack on the newly exposed grain boundaries. This process repeated until the whole particle was removed from the matrix.

The commercial β -Ti alloy had a microstructure that was significantly different from that of Ti-6Al-4V+10 wt% Mo. Figure 4.21 shows the microstructure of the commercial β -Ti alloy. Figure 4.21a shows that the microstructure seems very porous, but from Figure 4.21b at a higher magnification, it was evident that some of the sites which looked like pores with optical microscopy were actually sites with a different structure from the bulk of the microstructure, as highlighted by the red circle in Figure 4.21b.

The microstructure was characterized by columnar grains running parallel to the build direction. The wave-like structure observed in the Ti-6Al-4V+10 wt % Mo sample was also observed for the β -Ti alloy, but was less noticeable. The composition detected by EDX was slightly different for some elements (Ti, Al, and Cr) than specified by the manufacturer, although within errors, Table 4.1.

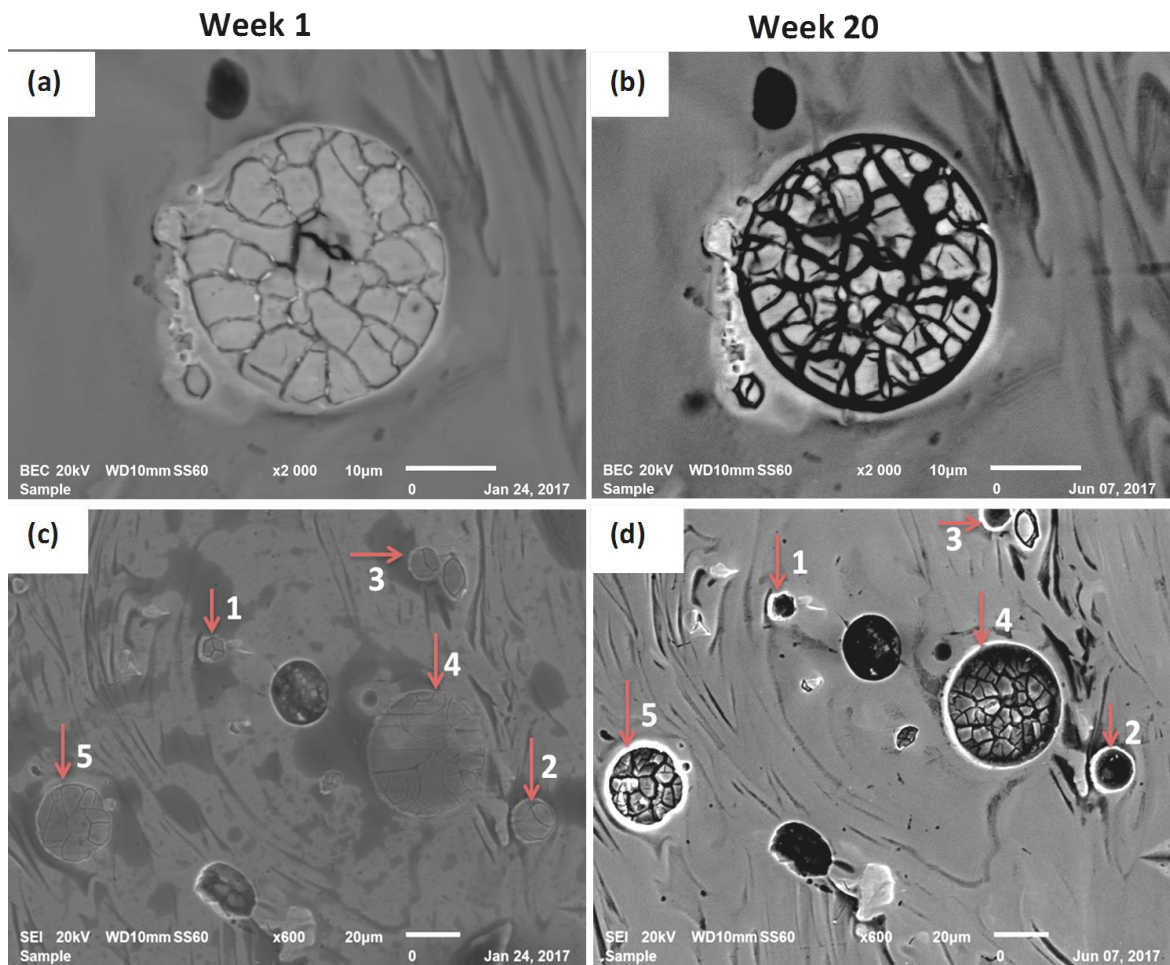


Figure 4.20: SEM BSE and SE images showing progression of corrosion: (a) and (c) high and low magnification images respectively after 1 week immersion, and (b) and (d) high and low magnification images respectively after 20 weeks immersion in 3.5% NaCl solution.

Table 4.4.1: Compositional analysis of β -Ti alloy.

Element	Expected composition (mass%) (Manufacturer's specifications)	EDS detected composition (mass%)
Ti	75	74 $\pm$ 2.8
Al	3	5 $\pm$ 1.4
V	8	8 $\pm$ 0.7
Cr	6	5 $\pm$ 0.7
Zr	4	4 $\pm$ 0.7
Mo	4	4 $\pm$ 0.7

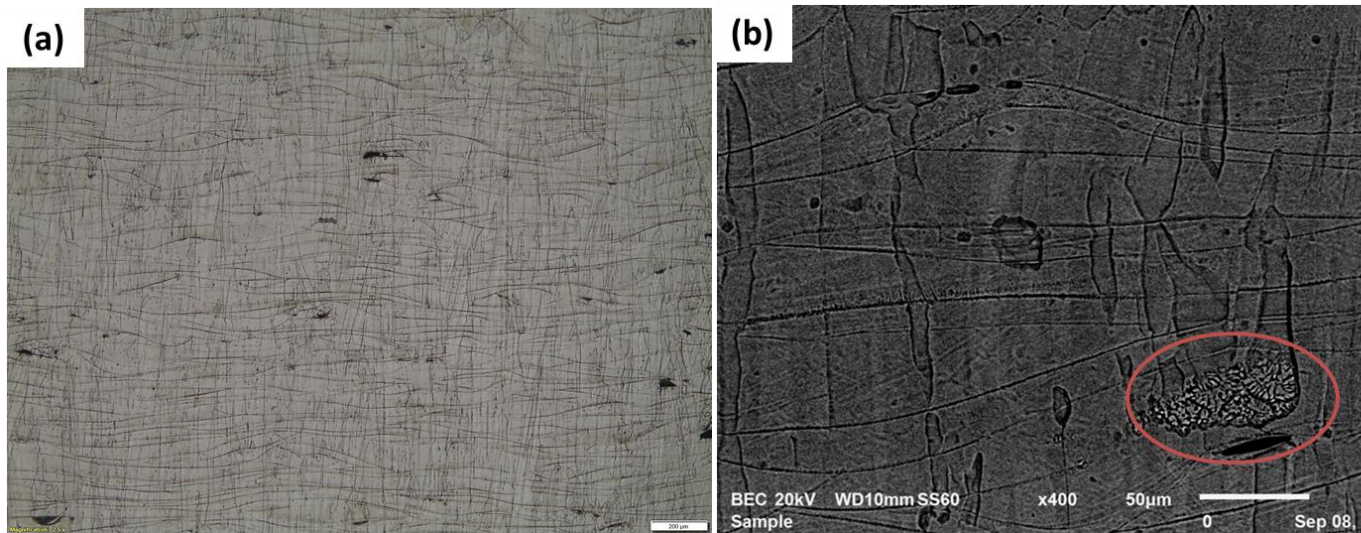


Figure 4.21: Microstructure of β -Ti alloy built at 1.3 kW power, 3 m/s speed and 50 % hatch overlap: (a) Optical micrograph (200 μ m micron bar) and (b) SEM-BSE micrograph (50 μ m micron bar).

Figure 4.22 shows the EBSD results of the β -Ti alloy, with the build direction from left to right. Figure 4.22a shows the area used for analysing the phases present and in Figure 4.22b the phase identified was cubic beta titanium. This was the only phase identified throughout the sample. Figure 4.22c shows the area used to examine the grain structure of the β -Ti alloy. The columnar grains identified in Figure 4.21 were clearly visible in Figure 4.22d. The sites highlighted by the red circle in Figure 4.21b were confirmed to have a different grain structure than the bulk of the material. The bulk of the material had elongated columnar grains, while these sites had smaller rounded grains clustered together. The wave-like structure separating different layers was not visible in Figure 4.22.

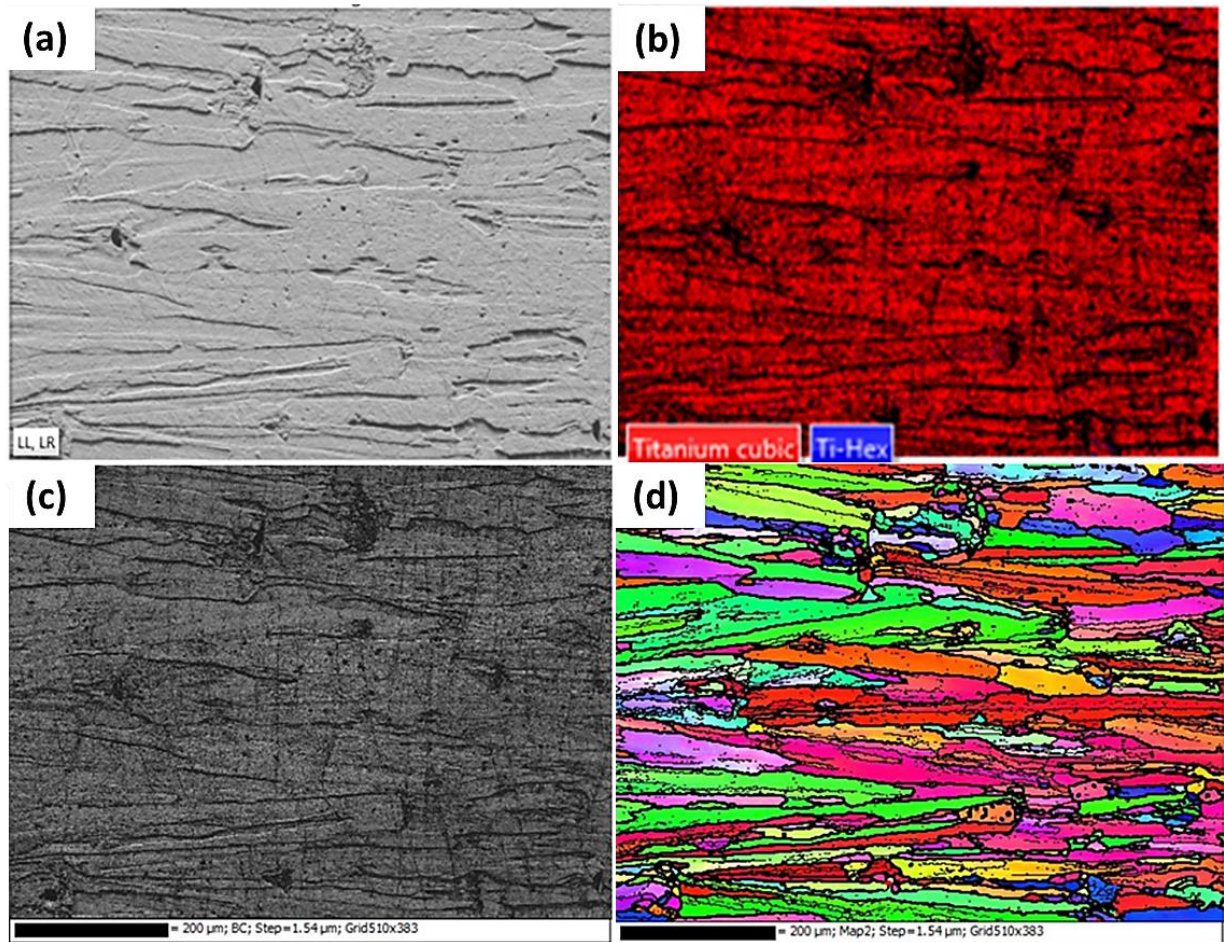


Figure 4.22: EBSD phase analyses (with build direction from left to right) of β -Ti alloy samples manufactured with the SLM machine: (a) area of analysis, (b) phase analyses, (c) area of analysis and (d) grain orientation map.

4.3.2 High power and high speed samples

Figure 4.23 shows the microstructure of Ti-6Al-4V built with the SLM machine (2 kW power and 2 m/s speed). The microstructure was characterized by columnar grains running parallel to the build direction (Figure 4.23a). Growing within these columnar grains were needle-like structures (Figure 4.23b). The EDX results confirmed the composition specified by the manufacturer.

Figure 4.24 shows the EBSD results for Ti-6Al-4V. Figure 4.24a shows the area used for analysing the phase present, and in Figure 4.24b, the major phase identified was martensitic α titanium. Figure 4.24c shows the area used to examine the grain structure and orientation of the Ti-6Al-4V alloy. Figure 4.24d shows that the needle-like feature grew nearly perpendicularly away from the edge of the columnar grains, towards the centre.

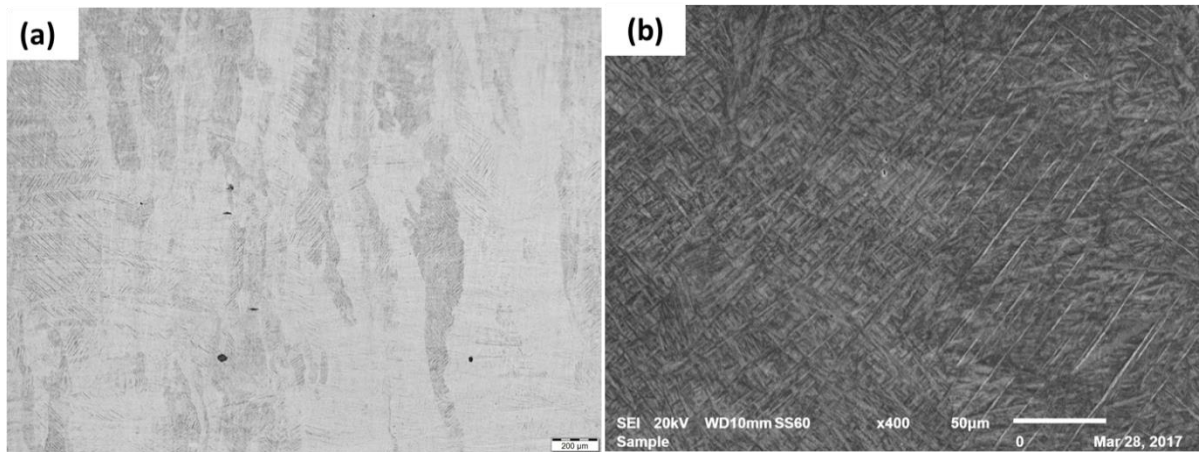


Figure 4.23: Microstructure of Ti-6Al-4V processed with the SLM machine built at 2 kW power, 2 m/s speed and 80 % hatch overlap: (a) Optical micrograph and (b) SEM-BSE micrograph.

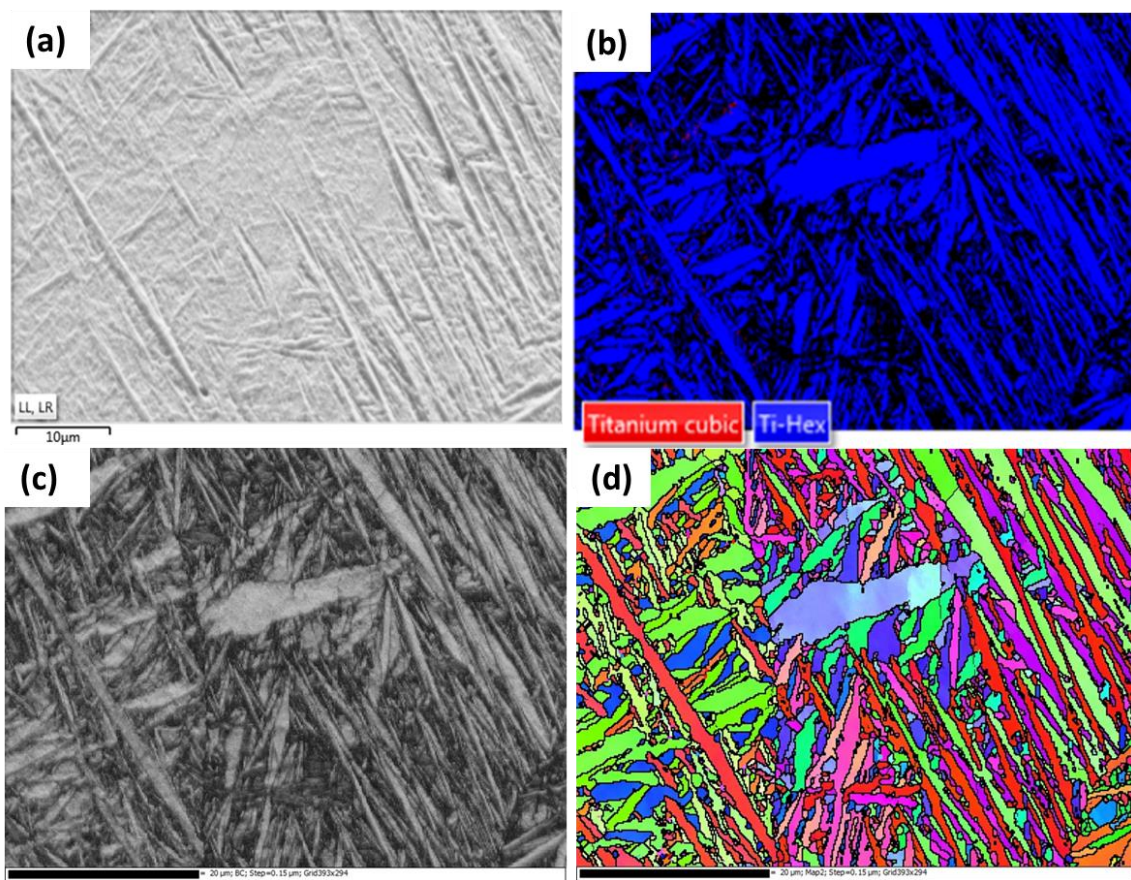


Figure 4.24: EBSD phase analyses with build direction from top to bottom of Ti-6Al-4V samples manufactured with the SLM machine: (a) area of analysis, (b) phase analyses, (c) area of analysis and (d) grain orientation map.

Figure 4.25 shows the microstructure of Ti-6Al-4V+10 wt% Mo alloyed *in situ* and manufactured at a higher power compared to that discussed in Section 4.3.1. No significant improvement in the microstructure was seen from the increase in power (1.3 to 2 kW) and

hatch overlap (50% to 80%), and the decrease in speed (2.5 to 2 m/s). The microstructure still comprised unmelted Mo particles, inconsistent Mo composition throughout the matrix (1 wt% dissolved in one area and 5 wt% dissolved in another area) and a wave-like structure separating each layer (Figure 4.25a). On the light bands, the EDX results showed a Mo content as high as 20%. Figure 4.25b revealed round and columnar grains growing across the melt pool boundaries.

Figure 4.26 shows the EBSD results performed on the Ti-6Al-4V+10 wt% Mo alloy. As found by the XRD results in Section 4.3.1, hexagonal titanium (α -Ti) and cubic structures (β -Ti) were present in the microstructure (Figure 4.26b). The hexagonal titanium structure was more prominent in the lath-like areas in the microstructure, while the cubic titanium structure was found in the smooth areas of the microstructure.

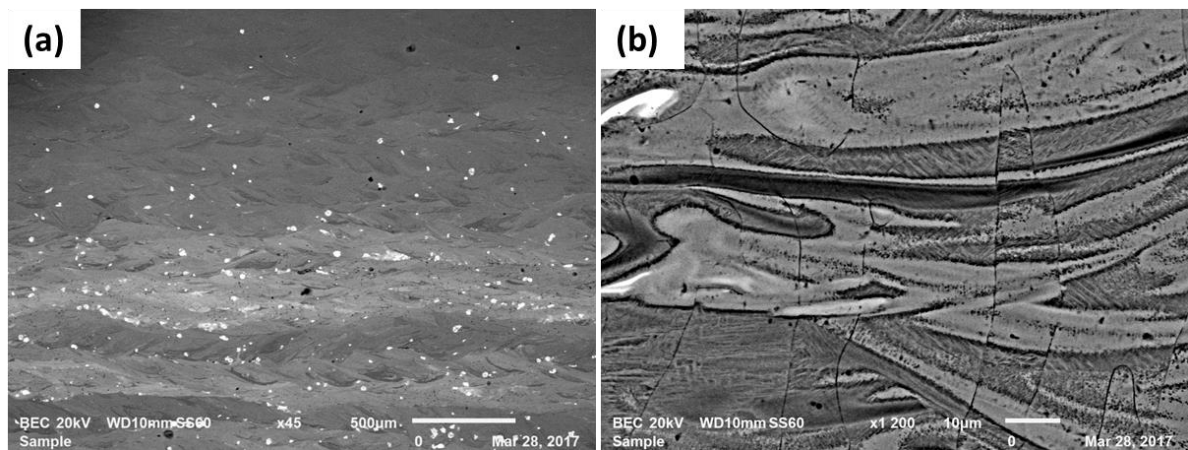


Figure 4.25: SEM-BSE images of Ti-6Al-4V+10 wt% Mo processed on the SLM machine built at 2 kW power, 2 m/s speed and 80 % hatch overlap.

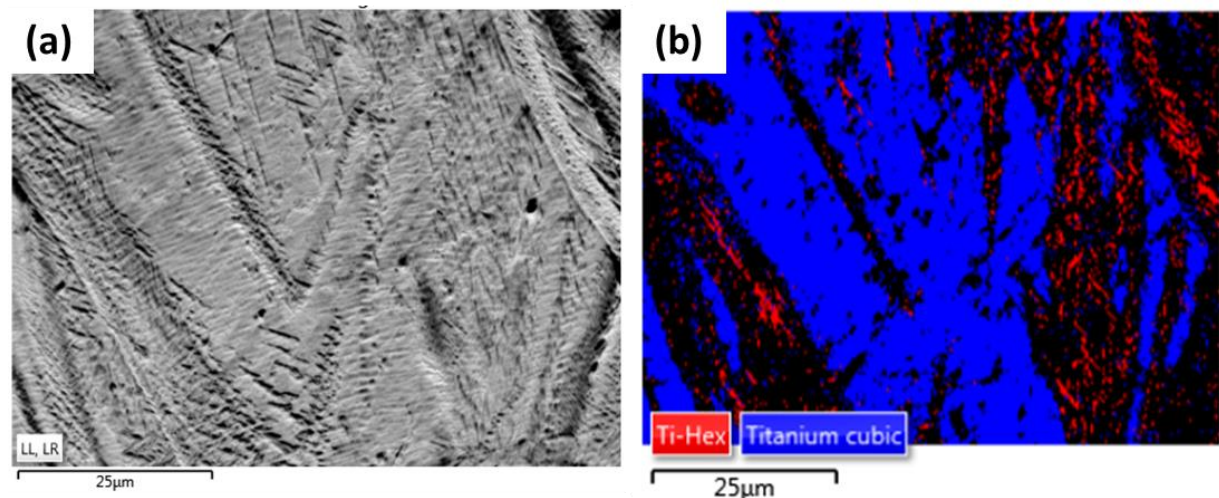


Figure 4.26: EBSD phase analysis results with build direction from top to bottom of Ti-6Al-4V+10 wt% Mo samples manufactured with the SLM machine built at 2 kW power, 2 m/s speed and 80 % hatch overlap: (a) area of analysis and (b) phase analysis.

4.3.3 Low power and low speed samples (LENSTTM DED)

When the same alloy (Ti-6Al-4V+10 wt% Mo) was alloyed *in situ* with the LENSTTM machine (DED), a different microstructure was obtained. Figure 4.27 shows the microstructure of the Ti-6Al-4V+10 wt% Mo alloy manufactured with the LENSTTM machine. Figure 4.27a shows a homogeneous microstructure where apparently almost all the Mo had dissolved bar one unmelted light particle. Figure 4.27b shows a microstructure comprising different size laths in a matrix. The EDS results showed a more homogenous composition than for the Ti-6Al-4V+10 wt% Mo samples manufactured by SLM. The dissolved Mo measured in the matrix ranged from 8 to 9 wt%. There were no areas which consisted of only of Ti-6Al-4V.

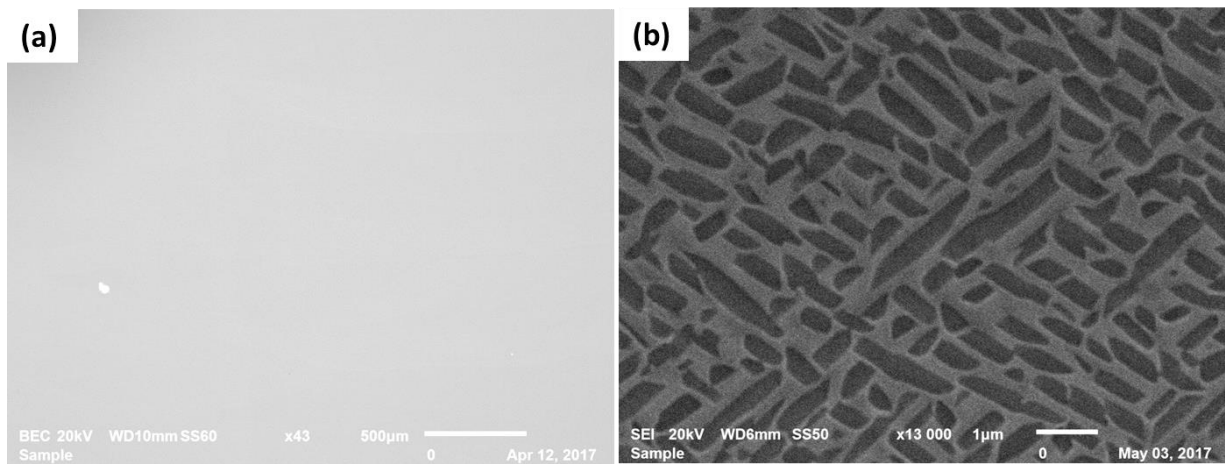


Figure 4.27: Microstructure of Ti-6Al-4V+10 wt% Mo manufactured on the LENSTTM machine built at 400 W power, 8.46 mm/s speed and 50 % hatch overlap: (a) SEM-BSE image, and (b) SEM-SE image.

Figure 4.28 shows the EBSD results of the Ti-6Al-4V+10 wt% Mo samples produced with the LENSTTM machine. The laths that were present in the microstructure (Figure 4.28a) had a hexagonal titanium structure (α -Ti phase) as identified in Figure 4.28b.

The microstructure of the Ti-6Al-4V+10 wt% Mo samples produced on the SLM machine did not meet the required standard in the as-built state, due to the lack of homogeneity. Unmelted Mo particles could not be avoided, and the inhomogeneity of the microstructure would make it harder to consistently reproduce the material (thus poor repeatability) which would not meet the stringent quality requirements of the aerospace industry.

The LENSTTM produced Ti-6Al-4V+10 wt % Mo samples gave promising results although a fully β microstructure was not obtained. The main purpose of this work was to obtain a suitable material for high power, high speed processing used by the AeroswiftTM (SLM)

machine. Therefore, the LENSTM samples only proved that for alloying samples *in situ* using different powders with such a large difference in melting points, a process that can give longer interaction time between the laser and the powder would be more appropriate.

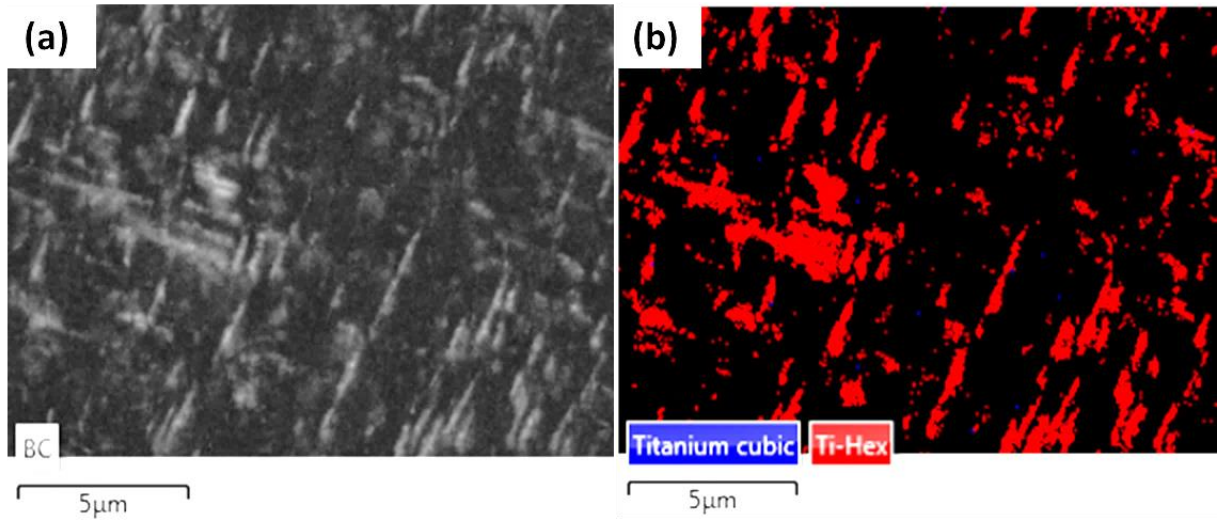


Figure 4.28: EBSD phase analysis results with build direction from top to bottom of Ti-6Al-4V + 10 wt% Mo samples manufactured with the LENSTM machine: (a) area of analysis and (b) phase analysis.

4.4 Mechanical Properties

For comparison, hardness was measured on all the samples to draw a more complete conclusion with regards to material suitability. Only the Ti-6Al-4V and β -Ti alloy samples were tensile tested, as it was important to investigate whether the β -Ti alloy could be a more suitable material compared to Ti-6Al-4V for high power, high speed PBF processing. For this reason, the parameters used for manufacturing Ti-6Al-4V were identical to the parameters chosen to build the commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) (1.3 kW power, 3 m/s speed and 50% hatch overlap).

4.4.1 Macro- and micro-Vickers hardness results

Figure 4.29 shows the average micro-hardness results obtained for a Ti-6Al-4V+10 wt% Mo (low power, high speed), Ti-3Al-8V-6Cr-4Zr-4Mo (β -Ti alloy) (low power, high speed), Ti-6Al-4V (High power, high speed) and Ti-6Al-4V+10 wt% Mo (high power, high speed) samples, all produced with the SLM machine. Also included in the results were the Ti-6Al-4V+10 wt% Mo samples produced with the LENSTM machine.

For samples produced on the SLM machine, Figure 4.29 shows that Ti-6Al-4V had a higher hardness than Ti-6Al-4V+10 wt% Mo produced at high power and high speed. The hardness of Ti-6Al-4V+10 wt% Mo produced at low power and high speed was lower than the

hardness of Ti-6Al-4V+10 wt% Mo produced at high power and high speed. The β -Ti alloy had a higher hardness than the Ti-6Al-4V+10 wt% Mo produced at low power and high speed. Ti-6Al-4V had a higher hardness compared to the β -Ti alloy. The Ti-6Al-4V sample produced on the LENSTM machine had a higher hardness than its SLM produced counterpart.

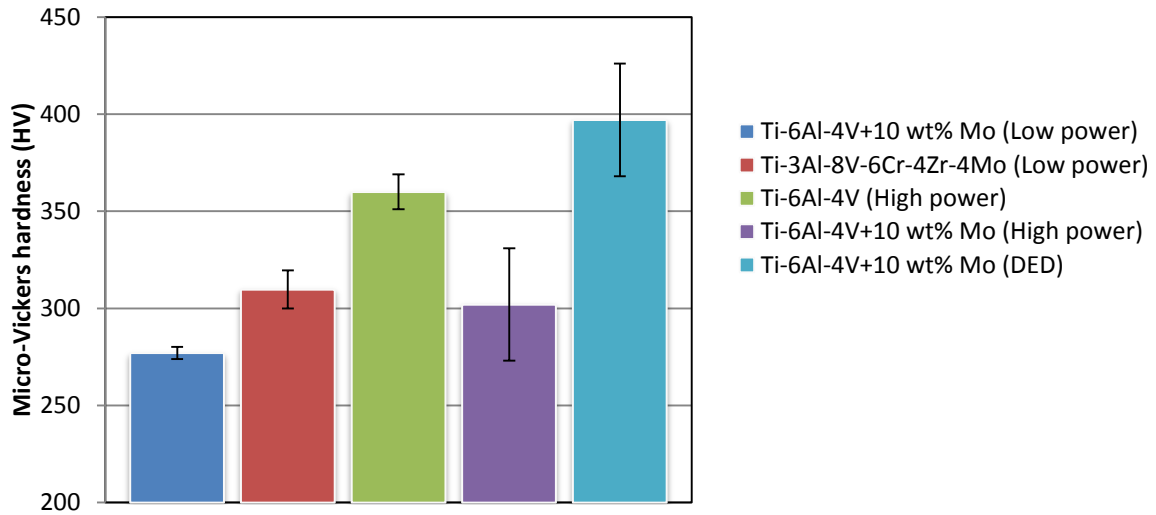


Figure 4.29: Comparison of micro-Vickers hardness results of samples built with the SLM and LENSTM machines.

For the Ti-6Al-4V+10 wt% Mo alloy, there was variation in the micro- and macro-hardness results. Figure 4.30 shows that the hardness value obtained was largely dependent on the area of indentation. A higher hardness was obtained (320 HV_{0.3}) when indenting on a Mo-depleted area, while a lower hardness was obtained (180HV_{0.3}) when indenting on a Mo-rich area.

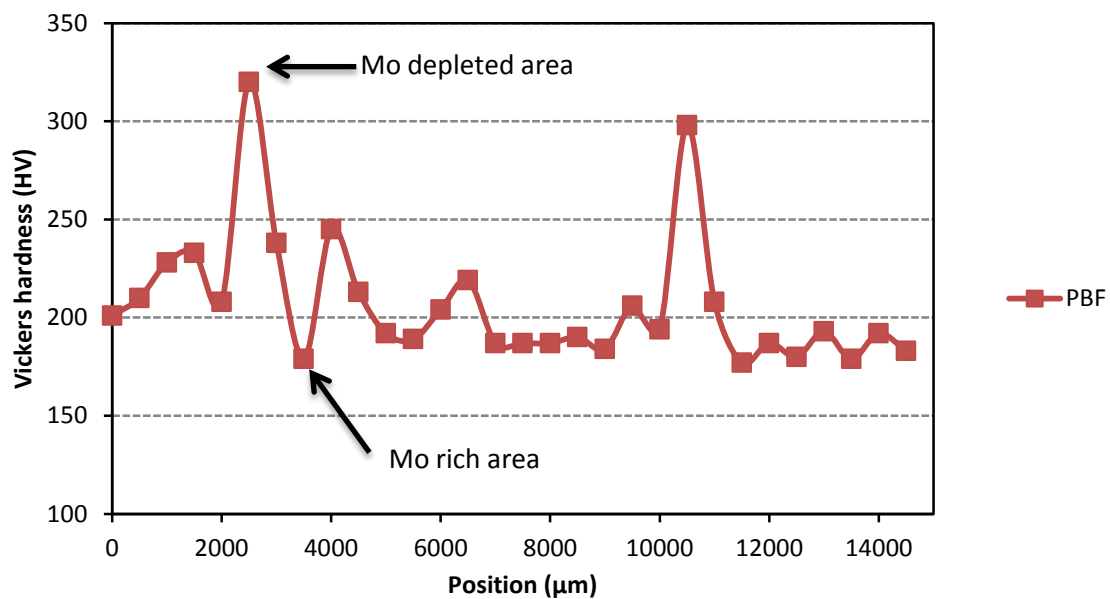


Figure 4.30: Micro-Vickers hardness results of Ti-6Al-4V+10 wt% Mo built with the SLM machine (hardness profile taken from top to bottom).

When macro-Vickers hardness tests were done, the hardness values were more stable as the indentation area was large enough to represent all the regions present in the microstructure. Figure 4.31 shows the macro-hardness results where the only visible variation exists from the hardness values obtained at the bottom to the top of the sample. The hardness at the bottom of the sample was lower than the hardness at the top of the sample

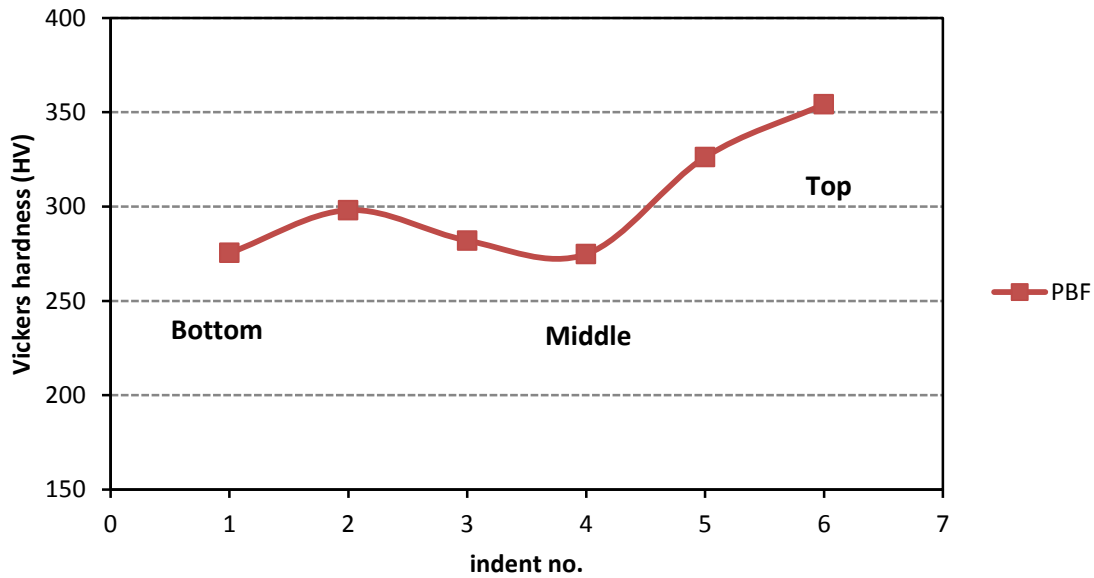


Figure 4.31: Macro-Vickers hardness results of Ti-6Al-4V + 10 wt% Mo built with the SLM machine.

4.4.2 Tensile results

One of the major disadvantages of additively manufactured parts is the anisotropy in mechanical properties. During tensile testing, not all directions could be tested because of sample size therefore the anisotropy could not be shown. Table 4.2 shows a summary of the tensile test results for Ti-6Al-4V and the commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo). The 0.2% proof stress and the UTS were higher for Ti-6Al-4V compared to Ti-3Al-8V-6Cr-4Zr-4Mo. Conversely, the elongation for Ti-3Al-8V-6Cr-4Zr-4Mo was found to be almost 3 times higher than for Ti-6Al-4V.

Figure 4.32 shows the stress strain curves generated for the two alloys (Ti-6Al-4V and β -Ti alloy). The area under each curve was calculated using the trapezium rule: for Ti-6Al-4V this area was calculated to be 2803.3 mm² and for the β -Ti alloy the area was 5454.3 mm². Thus β -Ti alloy had a larger area under the curve than to Ti-6Al-4V. This indicates that the β -Ti alloy had a higher fracture toughness than the Ti-6Al-4V, as the area under the curve gives an indication of the material's fracture toughness.

Examining the fracture surfaces of the two alloys in Figure 4.33, the fracture modes became evident. The Ti-6Al-4V alloy had a mixture of fracture modes: as seen in Figure 4.33a some areas show dimple-like fracture and in most areas cleavage fracture, while in Figure 4.33b the fracture surface of the β -Ti alloy contained only dimple-like fracture. The dimples in Figure 4.33b were more pronounced than those in Figure 4.33a, which appeared shallower. Internal porosity was evident in both alloys.

Table 4.2: Summary of tensile test results.

	Proof stress (0.2%) (MPa)	UTS (MPa)	Elongation (%)
Ti-6Al-4V	962.6 $\pm$ 2.0	1130.5 $\pm$ 7.0	9.0 $\pm$ 3.0
Ti-3Al-8V-6Cr-4Zr-4Mo	845.1 $\pm$ 1.0	863.4 $\pm$ 2.0	30.5 $\pm$ 3.0

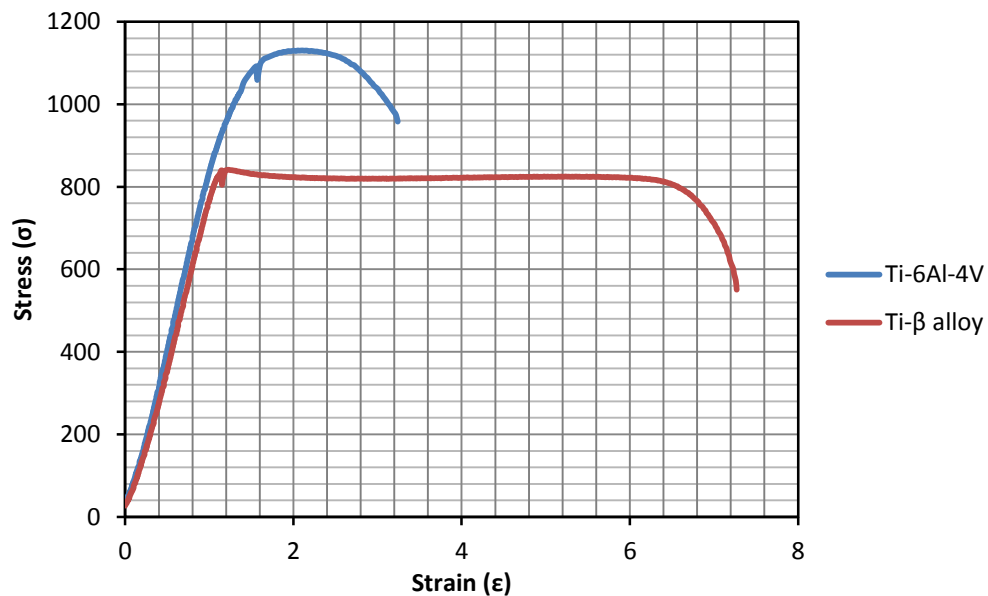


Figure 4.32: Stress/strain curves for Ti-6Al-4V (blue curve) and β -Ti alloy (red).

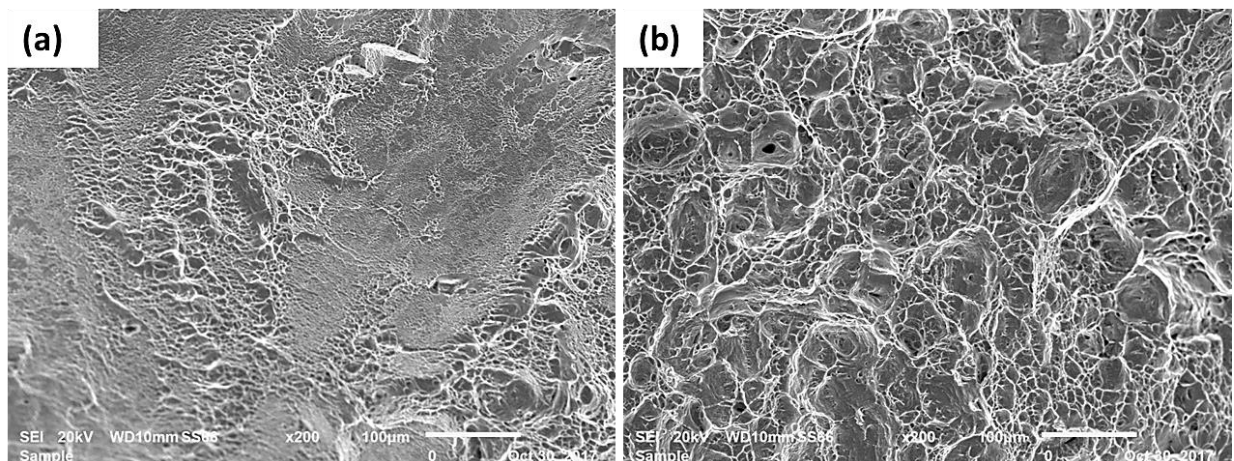


Figure 4.33: SEM-SE images of the fracture surfaces: (a) Ti-6Al-4V and (b) β -Ti alloy.

Chapter 5: Discussion

5.1 Effect of process parameters on build quality

Obtaining the right combination of process parameters was one of the main aspects of building high quality parts for the Ti-6Al-4V, Ti-6Al-4V+10 wt% Mo and Ti-3Al-8V-6Cr-4Zr-4Mo alloys. As reported in Section 4.2.2, energy density affected the amount and the shape of the porosity in the sample. This trend was true for all the samples built, regardless of alloy composition, although it was also observed that the effect of the energy density on the porosity was different for every alloy, this was due to the differences in alloy compositions, causing different behaviour, hence giving different trend lines and equations for the graphs (Figures 4.6, 4.8 and 4.11).

For Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo, the lowest porosity was found when utilising an energy density of 120.19 J/mm^3 . The density was 99.94% and 99.93% respectively. Thijs *et al.* (2010) found a relative density of 99.9% at an energy density of 93 J/mm^3 in their work on the selective laser melting of Ti-6Al-4V. While working on consolidating Ti with TiB reinforcements, Attar *et al.* (2014) found that an energy density of 120 J/mm^3 was sufficient to produce parts with relative densities higher than 99%. For Ti-3Al-8V-6Cr-4Zr-4Mo, the highest density of 99.6% was found at 69.3 J/mm^3 and 99.1 J/mm^3 . Therefore, the densities obtained were good in comparison to those found by Attar *et al.* (2014).

As the energy density increased, the sample porosity decreased and the shape of the pores changed. As a result of insufficient melting at low energy densities (less than 60 J/mm^3), unmelted powder particles were found inside the pores. Most of the pores occurred between build layers, due to insufficient heat being available for the adhesion of the previous layer to the newly-melted layer. At moderate to high energy densities (greater than 60 J/mm^3), the pores were more spherical and appeared smaller. These small pores resulted from gas bubbles and solidification shrinkage (Hao *et al.*, 2009). This agreed with Cherry *et al.* (2015) who found that the overall porosity in a 316L stainless steel sample was a strong function of laser energy density. At low energy densities, porosity was high. As the energy density increased the porosity decreased, only to increase again when excessive energy was added (Gunenthiram *et al.*, 2017; Cherry *et al.*, 2015; Kasperovich *et al.*, 2016).

The energy density trend was also observed by Kasperovich *et al.* (2016) who found that the shape of the pores obtained in a Ti-6Al-4V build was dependant on the energy density. Insufficient energy densities led to elongated, narrow, crack-like pores that formed perpendicular to the build direction, whereas at excessively high energy densities, the pores became more spherical with diameters less than 50 μm . These pores were most likely due to the keyhole effect (Kasperovich *et al.*, 2016), which was seen when the energy density was high enough to melt the powders and, in some cases, vaporise the metal. The keyhole has a sensitive equilibrium that easily becomes unstable when non-optimized parameters are used, therefore it could collapse and produce pores (Attar *et al.*, 2014).

5.2 Effect of adding Mo to Ti-6Al-4V on build quality

The build quality was defined according to the integrity of the sample. Samples with a good build quality would then be those that did not delaminate from the base plate, with no lack of fusion between build layers and were built to completion without spatter. To improve the properties of Ti-6Al-4V, specifically to avoid deformation and delamination of large parts from the base plate, it was important to investigate the effect of Mo addition on the build quality.

Figures 4.5 and 4.10 show that the addition of Mo to Ti-6Al-4V increased the size of the processing window in terms of the viable laser energy densities that could be used. As explained in Section 4.2.1, the samples that scored ‘1’ on the response curve:

- Did not delaminate from the base plate during manufacturing
- Manufacturing was not stopped due to spatter or uneven building
- Did not display severe lack of fusion between layers.

Those that scored a ‘0’ failed one of these evaluations.

When Ti-6Al-4V and Ti-6Al-4V+ 10 wt% Mo were plotted on the same axis (Figure 5.1), the effect of Molybdenum addition became clearer. At the lowest (32 J/mm^3) and highest (240 J/mm^3) energy densities (blue boxes), Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo failed the build quality test. In the red box, (48 and 64 J/mm^3) Ti-6Al-4V failed the build quality test, but with the addition of Mo, the samples passed the test. Therefore, under conditions where Ti-6Al-4V samples delaminated and failed the test, the addition of Mo caused the samples to adhere to

the base plate. With the addition of Mo, the build quality of some samples improved due to the refinement of the microstructure, and these samples could therefore be built to completion. In the purple box, Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo (93, 120 and 160 J/mm³) passed the build quality test. This identifies a processing window between 90 and 160J/mm³ where Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo were both successfully processed.

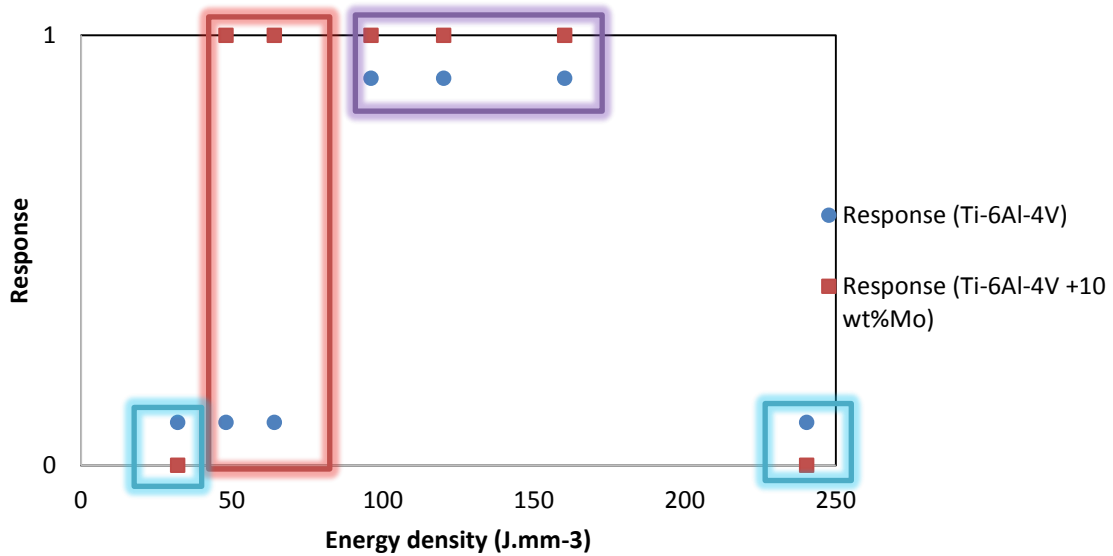


Figure 5.1: Graph showing effect of addition of Mo to Ti-6Al-4V on build quality test response.

5.3 Effect of process parameters on Mo dissolution

When trying to alloy two materials *in situ* with different melting points, finding optimum parameters became difficult. In Section 4.2.4.3, it was shown that manufacturing at lower speeds increased the dissolution of Mo. This was only true until a certain point, as the sample built at 2 m/s could not be completed due to spatter and a volatile melt pool, resulting in irregular scan tracks. The irregularity in the scan track was caused by the instability of the melt pool at very low speeds, where the melt pool hydrodynamics become more critical (Thijs *et al.*, 2010). There is no set speed where this happens, as the threshold depends on a combination of parameters. At low speeds, the interaction time between the powder and the laser increased, therefore allowing more Mo to dissolve.

At the highest speed, the lowest amount of Mo dissolved in the matrix. Fischer *et al.* (2016) alloyed Ti and Nb *in situ* on a SLM machine and also found a high number of unmelted Nb

powder particles when processing at high speeds. The maximum temperature on the surface increases with decreasing scan speed, while the track width decreases with increasing scan speed (Li *et al.*, 2009). The increased interaction time and area at lower scan speeds allowed more time for the heat (energy) to conduct throughout the material, therefore giving better melting of powder. Equation 2.1 shows that the speed is inversely proportional to the energy density; therefore a decrease in speed gives an increase in energy density. The increased interaction time was found to be essential in processing materials with such a large difference in melting points: Mo has a melting point of 2623°C and Ti-6Al-4V has a liquidus temperature of 1660°C (RSC, 2017). Thus, more time was needed to melt the Mo.

Increasing the hatch overlap improved the dissolution of Mo as shown in Section 4.2.4.4. Therefore, a hatch overlap of 80% means that a track was deposited to cover 80% of the previous track's width. Increasing the hatch overlap from 50% to 80% increased the peak temperature and decreased the temperature gradient as a result of the increased thermal accumulation, as found by Xia *et al.* (2016), which therefore resulted in better powder melting and Mo dissolution. A higher hatch overlap also leads to the migration of the molten liquid onto the previously fabricated tracks with a higher velocity, which causes the stacking of molten liquid (Xia *et al.*, 2016). As increasing the hatch overlap also leads to longer production times, this should be considered when choosing process parameters.

In Section 4.2.4.5, it was shown that an increase in power led to increased Mo dissolution. Referring to the energy density equation in Equation 2.1, increasing the power led to an increase in energy density. Therefore, more energy was available over the same area to melt more Mo powder, thereby increasing the Mo dissolution. Similar to the decrease in scan speed, the increase in power led to an increase in maximum temperature on the surface and an increased scan track width, but the increased influx density may induce vaporization of the powder and the balling effect (Li *et al.*, 2009). The balling effect occurs when molten powder fails to wet the base plate and high surface tension makes a spherical shape (Gong *et al.*, 2014). To avoid a bead-shaped surface, the power should be chosen with caution (Li *et al.*, 2009).

5.4 Comparison of samples produced on the SLM machine

The purpose of this work was to firstly alloy Ti-6Al-4V with Mo *in situ* to produce a β alloy with better mechanical properties than Ti-6Al-4V in the as-built state for high power and high speed SLM.

5.4.1 Microstructure of Ti-6Al-4V and Ti-6Al-4V + 10 wt% Mo (SLM)

From Section 4.3.2, the microstructure of Ti-6Al-4V comprised columnar grains growing parallel to the build direction and a fine needle-like structure growing inside these grains. The microstructure of Ti-6Al-4V was considered to be martensitic, mostly due to the high temperature gradients used during the powder bed fusion (PBF) process, as found by Thijs *et al.* (2010) and Murr *et al.* (2009). The phase analysis (Figure 4.24) identified α -Ti as the major phase. Due to the fineness and the crystal structure (hexagonal) of α -Ti in the microstructure, the type of α -Ti present was deduced to be α' .

From Figure 4.24d, α grains appear to be precipitating randomly within the β grain boundaries. This was identified as typical of the martensitic transformation as the α' grains form simultaneously from various points inside the β grain (Simonelli *et al.*, 2014a). The hardness of the microstructure, 360 ± 9 HV_{0.3}, also corresponded to the typical hardness values found for α' microstructure produced via PBF (Thijs *et al.*, 2010; Murr *et al.*, 2009). The columnar grains form due to the lack of further nucleation sites during solidification, and the grains grow epitaxially (Thijs *et al.*, 2010; Vrancken *et al.*, 2014; Devletian *et al.*, 1983).

From the grain orientation map (Figure 4.24d), there were regions where α' needles were aligned in the same direction and also regions where the needles seemed to be entangled in different directions in a basketweave-like structure. This entanglement was due to the competitive growth of α' needles (Simonelli *et al.*, 2012b). The α' needles differed in width and some also appeared longer than others, as a result of the grain size and the space available for growth. In addition, the size differences have been attributed to the build platform acting as a heat sink, therefore promoting variations in the grain growth of the α' needles (Simonelli *et al.*, 2014a). The α' needles grew within the prior β grains at different angles to the build direction, the majority growing at angles between $\sim 60^\circ$ and $\sim 80^\circ$. This result is consistent with other work involving the SLM of Ti-6Al-4V (Simonelli *et al.*, 2014a; Vrancken *et al.*, 2012). No explanation has yet been found to explain the preferred arrangement of α' martensitic laths (Banerjee and Williams, 2013; Simonelli *et al.*, 2014).

The Ti-6Al-4V+10 wt% Mo sample produced with the SLM machine was inhomogeneous. The goal was to replace α' needles with a fully β microstructure, but this was not achieved. Figure 4.23b shows the α' needles present in the Ti-6Al-4V microstructure, and the same α' needles were still found in some regions of the Ti-6Al-4V+10 wt% Mo microstructure (Figure 4.26a). The presence of these α' needles was confirmed by EBSD (Figure 4.26b), where this phase was more common in the crevice-like regions in the microstructure. The presence of Mo lowers the β transus temperature to 900°C, stabilizing the β phase at room temperature (Vrancken *et al.*, 2014). Unfortunately, the processing parameters were not conducive for complete stabilization of the β phase. The processing parameters for AeroswiftTM are for high build rates (building large parts fast), therefore not being able to *in situ* alloy Ti-6Al-4V with Mo means that other materials should be investigated for the machine. Vrancken *et al.* (2014) used slower speed (1600 mm/s) to allow better dissolution of Mo, hence obtaining complete stabilization of the β phase. Although better dissolution of Mo was obtained by Vrancken *et al.* (2014), undissolved Mo particles could not be avoided in the as built state, which is a micro-galvanic issue.

Due to the presence of Mo in the matrix, the β grains were shorter and wider compared to those in Ti-6Al-4V (Figure 4.25b). These grains propagated in the opposite direction to the maximum thermal gradient, which has been shown to be near the top centre of the melt pool (Vrancken *et al.*, 2014). Similar to results found by Vrancken *et al.* (2014), the addition of Mo changed the solidification mechanism from planar to cellular solidification, which changed the microstructure. Therefore, as the planar solidification led to large columnar β grains in Ti-6Al-4V, the change from planar to cellular solidification led to smaller elongated β grains growing aligned towards the centre of the melt pool in Ti-6Al-4V+ 10 wt% Mo.

Also found in the Ti-6Al-4V+10 wt% Mo microstructure were different contrasts (SEM backscattered images) of the matrix and unmelted Mo particles (Figure 4.25b). The contrasts of the matrix indicated different Mo compositions in the matrix and were due to the inconsistent melting of Mo throughout the sample. The variations in dissolved Mo content have been attributed to segregation within individual scan tracks (Chlebus *et al.*, 2015). The high speeds used in the SLM process were not sufficient to melt all the Mo powder and provide a homogeneous microstructure. This then led to a phase transition in the microstructure, where close to the partially melted and fully melted Mo particles, the region was fully β , and away from this area, there was an $\alpha + \beta$ region, and furthest away from the

dissolved particles, acicular α' phase existed. This phase transition contributed to the increase in the build processing window (Figure 5.1).

The large difference in the melting points of the two powders that were alloyed *in situ* was one of the major reasons for obtaining incomplete melting of Mo. A smaller particle size of Mo powder compared to the particle size for Ti-6Al-4V was used for the PBF processed samples, consistent with Vrancken *et al.* (2014), Chlebus *et al.* (2015), Sing *et al.* (2016) and Fischer *et al.* (2016) (Figure 4.1). However, inconsistent with the work of these authors, spherical Mo powder was used, as the only available stock of the supplier. The smaller size and irregular shape of refractory metal added increases their disposition to conglomerate (Vrancken *et al.*, 2014). The use of spherical Mo particles, instead of irregular shaped Mo particles, meant that the particles disposition to conglomerate decreased.

Vrancken *et al.* (2014) alloyed Ti-6Al-4V and 10 wt% Mo using the same PBF process, but at different parameters: lower power (250W) and speed (1600 mm/s). Although they reported that the microstructure was fully β , unmelted Mo particles in the as-build condition could not be avoided, and the light and dark bands also showed variations in undissolved Mo content that also could not be avoided (Figure 2.10a).

Fischer *et al.* (2016) also reported the presence of 1% unmelted Nb particles after alloying Ti *in situ* with 26 wt% Nb (Figure 2.10b). Vrancken *et al.* (2014) reported an unmelted Mo content of only 0.8 vol% and therefore could not detect any Mo peaks via XRD measurements. Conversely, Mo peaks were detected in this work in the XRD patterns (Figure 4.18) because the unmelted Mo content reached 2 vol.% at the slowest speed of 2.5 m/s (Figure 4.13).

The interaction time between the laser and the powder was identified as an important factor in obtaining the lowest amount of unmelted Mo particles. When working at high speeds such as 2 m/s and higher, the interaction times become shorter, resulting in an increase in unmelted particles. Vrancken *et al.* (2014) used a low processing speed of 1.6 m/s which gave Mo more time to properly dissolve into the matrix. Hence, less than 1% unmelted particles were reported. For high speed processing provided by the AeroswiftTM SLM machine, achieving such low values of unmelted Mo particles was not possible.

Molybdenum particles were inconsistently distributed throughout the matrix with more unmelted particles found at the bottom and centre of the sample compared to the top (Figure

4.25b). This could be attributed to the powder delivery system used by the POC2/SLM machine that was used, which is not automated so is prone to change due to human error, such as not delivering the correct amount of powder. On the other hand, the powder delivery system used by the larger AeroswiftTM system is automated, and should give more consistent results and uniform distribution of Mo particles than found by Vrancken *et al.* (2014). As the mass of Mo was lower (only 10 wt% added) than the mass of Ti-6Al-4V; this could have also affect the distribution of Mo in the overall mixed powder. From Figure 4.26b, the hexagonal titanium structure was more prominent in the lath-like areas in the microstructure. This was due to the process allowing less heat in those areas, therefore dissolving little to no Mo. The volatility of the melt pool could have also caused Ti-6Al-4V powder to be pushed to the boundary of the melt pool to the lath-like areas, while the bulk of Mo was dissolved in the inner smooth areas.

5.4.2 Micro-Galvanic corrosion of Ti-6Al-4V+10 wt% Mo

The degree of inhomogeneity of the Ti-6Al-4V+10 wt% Mo microstructure raised a concern with regards to the micro-galvanic effects. As mentioned in Section 2.7, in 3.5% NaCl solution, Ti-6Al-4V is number 85 on the galvanic series (Forman and Verchot, 1967) (Appendix A), while Mo is number 58. Therefore, the contact between these two metals would be conducive to micro-galvanic corrosion in the right environment.

Figure 4.19 shows that the microstructure of the unmelted Mo particles consisted of differently sized grains. Figure 4.19a shows that there were large pores in the powder, but from Figure 4.19b it is also evident that there were micro-pores between the grain boundaries. Inherent porosity can add to the process porosity and decrease the quality of the built samples (Cunningham *et al.*, 2017).

Figure 4.20 shows the progression of the micro-galvanic corrosion. The corrosion attack was mainly on the grain boundaries of the anodic Mo particles, due to the contact with the cathodic Ti-6Al-4V in the NaCl environment. The corrosion attack started on the surface of the Mo particles, and as the grain boundaries became more degraded, the grains became smaller. The corrosion attack continued until the corrosion layer lost its binding force, separated and fell out of the matrix, as also observed by Ping *et al.* (2017). After the layer fell off, another layer of the Mo particle was exposed and the corrosion attack followed a similar grain boundary attack until the whole Mo particle debonded from the matrix and fell out. This

type of attack on the grain boundaries has been identified as intergranular corrosion (Ping *et al.*, 2017).

The EDX results showed an increase in oxygen content of the corroded sample, as a result of the oxide corrosion product. Mo can be oxidized into molybdenum oxide (Ping *et al.*, 2017). A thin film of molybdenum oxide covered the surface of the alloy matrix, while some migrated into the NaCl solution. The corrosion attack was faster on the smaller Mo particles compared to the larger Mo particles. As discussed by NPL (2007), this was due to the area ratio: where the cathodic area was larger than the anodic area, the oxygen was reduced more easily, thereby increasing the galvanic current and the rate of corrosion.

Dai *et al.* (2016) studied the corrosion behaviour of a selective laser melted Ti-6Al-4V alloy in NaCl solution. In their work, the SLM-produced Ti-6Al-4V alloy showed inferior corrosion resistance to traditionally manufactured commercial Grade 5 Ti-6Al-4V. This was attributed to the presence of the large fraction of acicular α phase compared to the β -Ti phase. In the current study, the presence of Mo and its ability to stabilize the β phase was supposed to improve the corrosion properties of Ti-6Al-4V, but with the inhomogeneity in the microstructure, it introduced new problems. Therefore, further corrosion work needs to be done on the Ti-6Al-4V+10 wt% Mo alloy e.g. electrochemical measurements and polarization tests. Vrancken *et al.* (2014) did not consider the micro-galvanic effects when *in situ* alloying Ti-6Al-4V with Mo.

5.4.3 Vickers hardness of Ti-6Al-4V and Ti-6Al-4V+10 wt% Mo

Despite the level of microstructural inhomogeneity found in the Ti-6Al-4V+10 wt% Mo samples, the lower hardness results showed that the alloy was softer than the Ti-6Al-4V alloy produced under the same manufacturing parameters. Figure 4.29 shows that the hardness of Ti-6Al-4V (360 ± 9 HV_{0.3}) was nearly 20% higher than the hardness of Ti-6Al-4V+10 wt% Mo (302 ± 29 HV_{0.3}) produced at the 2 kW, 2 m/s and 80% hatch overlap. The Ti-6Al-4V α' martensitic microstructure is associated with brittleness and therefore high hardness values, compared to wrought Ti-6Al-4V which has a globular β in α matrix (Xu *et al.*, 2015). Addition of Mo led to softening of the microstructure, due to the increased β phase field provided by the Mo dissolved into the matrix, and its ability to stabilize β .

Vrancken *et al.* (2014) and Fischer *et al.* (2016) observed the same softening effect upon addition of a β stabilizer. Vrancken *et al.* (2014) also reported an increase in fracture strain, i.e. higher ductility (from $7.3 \pm 1.1\%$ to $20.1 \pm 2\%$) when comparing Ti-6Al-4V with Ti-6Al-

4V+10Mo. The lower hardness reported for the Ti-6Al-4V+10 wt% Mo sample suggests that even though the microstructure was not fully β , the $\alpha+\beta$ + Mo microstructure could give a higher fracture toughness value than Ti-6Al-4V, but a lower fracture toughness compared to Vrancken *et al.* (2014) who managed to achieve a fully β microstructure.

Due to the inhomogeneity of the Ti-6Al-4V+10 wt% Mo microstructure, there was variation in the micro-hardness results. The hardness value was largely dependent on the indentation area. As mentioned in Section 5.4.1, there were areas of varying Mo content in the microstructure. Therefore indenting on a Mo-rich area gave lower hardness compared to indenting on a Mo-depleted area, as shown in Figure 4.30.

The hardness of Ti-6Al-4V+10 wt% Mo produced at low power and high speed was lower than the hardness of Ti-6Al-4V+10 wt% Mo produced at high power and high speed. The Ti-6Al-4V +10 wt% Mo produced at high power and high speed were produced at a higher energy density (160.3 J/mm^3), compared to the low power, high speed samples (83.2 J/mm^3). It was expected that the samples manufactured at the high energy density would give a higher hardness compared to the samples manufactured at a lower energy density, due to better Mo dissolution in the Ti-6Al-4V +10 wt% Mo alloy. The micro-hardness results depended largely on the indentation area, therefore the lower hardness was more a reflection that more indentations were made in Mo-rich areas.

For the macro-Vickers hardness results, more representative hardness values were obtained due to the higher load used during testing, as the larger indentation was able to cover both Mo-rich and Mo-depleted areas. The only variation in these results was the difference in the hardness values from top to bottom of the sample, as shown in Figure 4.31. This was due to more heat being conducted to the bottom and centre of the sample, compared to the top of the sample, resulting in more Mo dissolved at the bottom than the top. Liu *et al.* (2017) reported that the cooling rate of the upper surface of the sample ($\sim 1.44 \times 10^6 \text{ K/s}$) was higher than the cooling rate at the bottom of the sample ($\sim 1 \times 10^3 \text{ K/s}$), which affected the microstructure formed in the component, and therefore affected the mechanical properties. However this effect is dependent on the thickness of the part, therefore only the top part of the sample shows a significantly higher hardness. The difference in the cooling rate from the bottom to the top of the sample in PBF processing leads to more Mo being dissolved at the bottom and the middle than at the top, leading to the variation in hardness values.

Since the Ti-6Al-4V samples were built from pre-alloyed powder, the hardness results did not depend on the dissolution of one element as was the case with the alloy produced via *in situ* alloying. Therefore, although the difference in cooling rates from the bottom to the top of the sample also affected the Ti-6Al-4V microstructure, the extent was negligible, as there was not much variation in hardness.

As a result of the degree of inhomogeneity in the as-built microstructure, and the micro-galvanic corrosion effects, no further investigations were done on this alloy manufactured with the SLM machine. Rather, as the interaction time was one of the factors that greatly influenced the melting of Mo, a DED machine that provided increased interaction times like the LENSTM was considered.

5.5 Comparison of Ti-6Al-4V+10 wt% Mo produced by SLM and LENSTM

Unlike the SLM machine, the LENSTM machine can produce samples at very low speeds, giving the Mo-powder enough time to melt. As discussed in Section 5.4.1, Figure 4.25b shows an inhomogeneous microstructure of the alloy produced with the SLM machine. The microstructure was characterized by unmelted Mo particles and varying dissolved Mo content throughout.

5.5.1 Microstructural comparison

Comparing the Ti-6Al-4V+10 wt% Mo microstructure produced with the SLM machine to the sample produced with the LENSTM machine shown in Figure 4.27a, there was a vast difference. There were nearly no unmelted particles in the alloy matrix of Ti-6Al-4V+Mo and the microstructure showed improved homogeneity. The microstructure also had a smooth alloy matrix (Figure 4.27a), with no visible scan tracks, contrary to those evident in the PBF samples produced on the SLM machine (Figure 4.25a).

The speed used during the DED process (0.008 m/s) was much lower than the speed used in the PBF process (2 m/s), hence giving longer interaction times between the laser and the powder, and therefore better melting of Mo. Although better melting of Mo was achieved, the process parameters changed the evolution of the microstructure. Instead of obtaining a fully β microstructure, as Vrancken *et al.* (2014) reported, there were shortened α laths present. Vrancken *et al.* (2014) mentioned that in order to fully stabilize the β phase, 10 wt% Mo needed to be added to Ti-6Al-4V. This seemed to be true for the PBF process, but not for the DED process. Figure 4.27b shows that the DED microstructure was characterized by

shortened α laths in a β matrix. The proportion of alpha precipitates was larger than the proportion of the β matrix. This indicates that with the addition of 10wt% Mo, the β phase was not stabilized. With the addition of more Mo, the size of α laths decreased and more of the β phase was stabilized (Figure 2.8), as observed by Collins *et al.* (2003).

5.5.2 Vickers hardness comparison

The Ti-6Al-4V+10 wt% Mo alloy produced with the SLM machine had a much lower macro-hardness (302 ± 29 HV_{0.3}) than the alloy produced with the LENSTM machine (397 ± 29 HV_{0.3}). This could be attributed to the dispersion of α laths in the microstructure which have a hardening effect, while the presence of Mo in the PBF samples (although not fully dissolved) had a softening effect. The amount of dissolved Mo was high enough to stabilize the β phase in most areas, hence reporting a lower hardness than Ti-6Al-4V. As confirmed by Collins *et al.* (2003), who alloyed commercially pure Ti *in situ* with Mo by DED, the increased interaction time of the DED process changed the solidification process and introduced two solid state transformation processes. These were the precipitation of secondary α laths inside the retained β phase region, and then the re-precipitation of β on the primary α laths and β matrix interface that produced secondary laths, which ultimately became equiaxed α precipitates, similar to the microstructure seen by Collins *et al.* (2003). Therefore, the high hardness in the DED-produced samples was due to α laths and β matrix solidifying with non-equilibrium compositions, resulting in the α laths being supersaturated in Mo and the β phase being under-saturated in Mo at room temperature as described by Collins *et al.* (2003). The higher hardness could also be attributed to the finer microstructure. The smaller grains give a greater ratio of grain boundary to dislocations therefore resulting in greater material strength (Hall-Petch effect) (Hansen, 2004).

The increase in hardness with the addition of Mo via the DED process could also be due to ω precipitates present in the matrix (Collins *et al.*, 2003). The ω phase rejects β stabilizing elements, making it possible for these precipitates to act as heterogeneous nucleation sites for precipitation of the equilibrium α phase (Devaraj *et al.*, 2009a). This would lead to a homogeneous distribution of refined α precipitates that significantly strengthens the alloy (Devaraj *et al.*, 2009a).

Athermal ω precipitates that form during quenching from β solution temperatures are known to take on the composition of the parent β matrix (Devaraj *et al.*, 2009b). This could explain why the EBSD results of the DED sample (Figure 4.28b) were not able to detect any cubic

phase, *i.e.* beta titanium, as the matrix consisted of the homogeneously distributed ω phase that inherited the composition of the β phase or the β phase could have been so finely distributed that it was difficult to resolve by EBSD. The presence of the ω phase can be confirmed using TEM (Collins *et al.*, 2003). Collins *et al.* (2003) reported that hardness increased up to a maximum of 450 HV_{0.3} with addition of 18.2 wt% Mo, while the lowest hardness value of 280 HV was obtained with the addition of 33.4 wt % Mo.

Although the DED process produced a more homogeneous microstructure compared to the PBF process, the amount of Mo needed to obtain a fully β microstructure was more than that needed to obtain same softening effect in the PBF process. Post-build heat treatment could give a homogeneous microstructure, as shown by Vrancken *et al.* (2014). Therefore, the question of which process would be better for alloying Ti-6Al-4V *in situ* with Mo would need a cost investigation, considering the cost of post heat treatment for the SLM process and the increased Mo powder needed for the DED process to obtain the same softening effect.

5.6 The commercial β -Ti alloy as an alternative

Reflecting on the main aim of this work, which was to produce an alloy with better fracture toughness and ductility compared to Ti-6Al-4V for PBF processing in the as-built state, the Ti-6Al-4V+10 wt% Mo did not meet the required properties. Due to the difficulty of obtaining commercial titanium alloy powder, being able to alloy *in situ* from elemental powders that were readily available would have been more beneficial. Since that was unsuccessful, a rod of a commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) with better ductility than Ti-6Al-4V was procured in the USA and then gas atomised in Germany (Figure 4.2). The β -Ti alloy is currently used for fasteners, springs, torsion bars and foil (Matweb, 2017), and it was the only alloy available in an affordable quantity.

5.6.1 Comparing commercial β -Ti alloy with Ti-6Al-4V

Figure 4.21 shows that the microstructure of the β -Ti alloy consisted of columnar β grains running parallel to the build direction. It was also noted that the wave-like structure observed for the Ti-6Al-4V+10 wt% Mo sample produced on the SLM machine was also present in the β -Ti alloy. Therefore, the wave-like structure, described as the melt pool boundaries by Vrancken *et al.* (2014), was a characteristic of processing material that was more ductile than Ti-6Al-4V, where this phenomenon was not observed. The materials with higher ductility are more viscous (create a more volatile melt pool), therefore the high cooling rates favour the

creation of these boundaries. This phenomenon could also be caused by the processing parameters not being optimized.

Comparing the microstructure of Ti-6Al-4V and that of the commercial β -Ti alloy, the acicular α' growing in prior β grains found in Ti-6Al-4V was not present in the commercial β -Ti alloy. The commercial β -Ti alloy was characterized by elongated β grains growing in the same direction as the build direction (Figure 4.21). According to Vrancken *et al.* (2014), Schwab *et al.* (2016) and Thjis *et al.* (2010), these elongated grains grew through epitaxial growth, where the previously solidified layer acts as nucleation sites. This was typical of samples manufactured by PBF process.

The Ti-6Al-4V alloy only has vanadium as a β stabilizing element, whereas in addition to vanadium, the commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) has molybdenum and chromium as β stabilizers. Aluminium was the only α stabilizing element in the alloy. Vrancken *et al.* (2014) reported that Zr destabilizes the planar solidification front without affecting the α and β phases; this could explain the role of zirconium in the commercial β -Ti alloy. The higher proportion of β stabilizers than α stabilizers in the commercial β -Ti alloy allows for more of the β phase to be stabilized than in Ti-6Al-4V.

Figure 4.21b shows there were regions in the microstructure which had rounded grains clustered together. The grains in these sites exhibited cellular grain growth. As confirmed by Schwab *et al.* (2016), the change in solidification morphology from planar to cellular and cellular-dendritic structures was due to the destabilization of the planar solidification as a result of the changing ratio of the thermal gradient and solidification rate.

Comparing the mechanical properties of the Ti-6Al-4V and the commercial β -Ti alloy, it was evident that the β -Ti alloy (309 ± 9 HV_{0.3}) was softer than Ti-6Al-4V (360 ± 9 HV_{0.3}). This was expected as the bcc crystal structure is softer than the hcp crystal structure phase. From Table 4.2, the yield stress and ultimate tensile strength (UTS) of Ti-6Al-4V were higher than those for the commercial β -Ti alloy, but the elongation of the commercial β -Ti alloy was higher than for Ti-6Al-4V. An increase in toughness (area under the curves in Figure 4.32) was accompanied by a decrease in strength.

Ductile fracture was the dominant fracture mode found when examining the fracture surface of the β -Ti alloy and Ti-6Al-4V. As confirmed by Xu *et al.* (2015), the presence of elongated prior β grain boundaries and acicular α' martensite in the microstructure of Ti-6Al-4V induced

intergranular failure. The elongation of Ti-6Al-4V was found to be below 10%. Therefore, as built PBF produced Ti-6Al-4V does not qualify to be used in critical structural applications (Xu *et al.*, 2015).

The tensile properties of the samples can be different in all directions, i.e. they are anisotropic, and this is common in PBF processing (Dieter, 1988). The properties most affected by a change in orientation are the yield strength, and to some extent, the tensile strength (Dieter, 1988). The tensile samples in the current work were built and tested in the XY direction (longitudinal direction). Horizontally built samples (XY) exhibit high strength properties and lower ductility compared to vertically built samples (XZ) during tensile testing (Simonelli *et al.*, 2014b; Popovich *et al.*, 2017). Therefore, the elongation of 30% would have been higher if the samples had been built in the XZ and ZX direction, and the strength would have been lower. Simonelli *et al.* (2014b) noted that the low elongation value in the XY direction compared to the XZ and ZX directions could be due to the samples having more defects (voids). Curling of PBF parts is caused by thermal stresses that build up in samples built in the XY direction, and curling leads to uneven powder deposition, which causes the formation of pores (Simonelli *et al.*, 2014b). Therefore, samples need to be built in the ZX and XZ directions in order to get a better understanding of the tensile properties.

5.6.2 Comparing β -Ti alloy with Ti-6Al-4V+10wt% Mo alloyed *in situ* on SLM machine

The hardness of the β -Ti alloy is the same within the experimental errors as the hardness of Ti-6Al-4V+10 wt% Mo (309 ± 9 HV_{0.3} and 302 ± 29 HV_{0.3} respectively). The hardness of the β -Ti alloy (309 ± 9 HV_{0.3}) was lower than Ti-6Al-4V+10 wt% Mo (338 ± 5 HV_{0.3}) produced by Vrancken *et al.* (2014). The UTS of the β -Ti alloy (863.4 ± 2.0 MPa) was ~6% lower than that of Vrancken *et al.* (2014) (919 ± 10 MPa), whereas the elongation of the β -Ti alloy was higher (30 %) than Vrancken *et al.*'s (2014) alloy (20.1 ± 2.0 %). The β -Ti alloy was more ductile than the alloy (Ti-6Al-4V+10 wt% Mo) alloyed *in situ*, with only a small decrease in UTS. The difference in ductility can be attributed to the higher proportion of β stabilizing elements in the β -Ti alloy (β phase is softer than α phase).

5.6.3 Comparing PBF β -Ti alloy with β -Ti alloy produced via casting

The solution treated (815°C) and aged (565°C) β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) produced via casting had a higher UTS of 1240 MPa but a lower elongation of 7% (Boyer *et*

al., 1998), when compared to the PBF β -Ti alloy (UTS = 863.36 ± 19 MPa and elongation = $30 \pm 3\%$). The difference in mechanical properties was due to the different microstructures. The β grains in PBF-produced β -Ti alloy were elongated, while the β grains of cast and solution treated β -Ti alloy were equiaxed with fine α precipitates, as found by other authors (Boyer *et al.*, 1998; Lukaszek-solek, 2015; Berg *et al.*, 1998). The equiaxed β (fine) grains and α precipitates made the alloy stronger than the PBF alloy which contained only columnar β grains and no α . The ageing process also made the cast alloy stronger, due to the hardening effect, as opposed to the PBF samples which were not heat treated.

5.6.4 Comparing β -Ti alloy with Ti-5Al-5Mo-5V-3Cr

Schwab *et al.* (2016) identified a near- β Ti-5Al-5Mo-5V-3Cr alloy as having good ductility and high strength, which could be used in the aerospace industry. They reported that the alloy produced via the PBF process had a tensile strength of 800 MPa and a total strain of up to 14%. Comparing the near- β alloy (Schwab *et al.*, 2016) with the β alloy studied in this work, it was evident that Ti-3Al-8V-6Cr-4Zr-4Mo exhibited higher strength (845 ± 13 MPa), and more than twice the ductility of 30% offered by the near- β alloy.

Ti-3Al-8V-6Cr-4Zr-4Mo shows great potential as a suitable alloy for PBF processes. The high ductility of the alloy is expected to make the alloy better suited to deal with the high residual stresses that caused the Ti-6Al-4V alloy to fail (delaminate from the base plate) during the manufacturing of large parts.

Chapter 6: Conclusions

Improving the ductility and fracture toughness of as-built Ti-6Al-4V parts by PBF processing via *in situ* alloying was considered as being important for the manufacturing of large parts, because they delaminated from the base plate as a result of the Ti-6Al-4V acicular α' microstructure that had poor ductility (<10%). Consequently, the parts were not able to withstand the residual stresses during manufacturing. Being able to increase the ductility of Ti-6Al-4V *in situ* by the addition of a β stabilizing element, such as Mo, would save time and would allow for the customization of the alloy to better suit high power, high speed PBF processing.

6.1 Summary of findings

The Ti-6Al-4V+10 wt% Mo alloy produced with the selective laser melting machine had an inhomogeneous microstructure with unmelted Mo particles and variation of dissolved Mo in the matrix. This was due to the short interaction times afforded by the high power, high speed PBF process. This inhomogeneous microstructure resulted in inconsistent hardness results; indenting on an area with more dissolved Mo led to a lower hardness (180 HV_{0.3}) than indenting on an area with depleted Mo (320 HV_{0.3}). For this reason, no other mechanical tests were carried out on this alloy.

It was still worthwhile to investigate how *in situ* alloying on the LENSTM machine would affect the microstructure of this alloy, with the longer interaction times afforded by the machine. The microstructure consisted of α laths in a β matrix, with negligible unmelted Mo particles. The presence of α laths and the possibility of the presence of the ω phase in the matrix led to a high hardness (397 $\pm$ 9 HV_{0.3}). The amount of Mo needed to fully stabilize the β phase for the directed energy deposition process was found to be higher than that needed for the powder bed fusion process.

Since modifying Ti-6Al-4V *in situ* by adding Mo was unsuccessful, using a commercial β -Ti alloy powder with increased ductility was the best alternative for high power, high speed PBF processing. The microstructure of the commercial β -Ti alloy consisted of elongated β grains with no α . The hardness of the commercial β -Ti alloy (309 $\pm$ 9 HV_{0.3}) was lower than for Ti-6Al-4V (360 $\pm$ 9 HV_{0.3}). The fracture toughness and ductility of the commercial β -Ti alloy was

higher than for Ti-6Al-4V, but the UTS of Ti-6Al-4V was higher than the commercial β -Ti alloy. The fracture surface of the commercial β -Ti alloy and Ti-6Al-4V had characteristics of ductile fracture.

6.2 Main conclusions

In this work the following conclusions were made:

- *In situ* alloying for high power, high speed PBF processing is not feasible due to the short interaction times afforded by the process which did not fully melt Mo.
- The micro-galvanic corrosion effects of the inhomogeneous microstructure need to be considered when using the alloy in the as-built state for application in corrosive environments.
- A homogeneous microstructure was obtained by the DED process, although more Mo would be needed to stabilize the β phase and the longer interaction times might be beneficial for full dissolution of Mo, but not beneficial for high production rates.
- 10% Mo is not a good choice to use as beta stabilizer for *in situ* alloying with Ti-6Al-4V. Using 10 wt% Mo with high power, high speed PBF does not fully melt all the Mo, results in an inhomogeneous structure and does not produce a fully beta alloy. With DED, more than 10 wt% Mo would be required to obtain a fully beta alloy.
- The commercial β -Ti alloy was found to be better suited for making large parts for high power, high speed processing due to the increased ductility that is expected to withstand the residual stresses that cause Ti-6Al-4V parts to delaminate.

6.3 Summary of contributions

This research has added to the existing body of knowledge by outlining that *in situ* alloying for high power, high speed PBF processing is not successful, especially for alloying elements with a large difference in melting points. This means that modification of materials and alloy development *in situ* cannot be accomplished without post processing, especially when making parts for the aerospace industry, which has stringent quality demands.

The micro-galvanic corrosion of such an inhomogeneous microstructure (unmelted Mo particles in a Ti-6Al-4V and Ti-6Al-4V+Mo matrix) was researched for the first time in this

work. This means any possible application of the alloy in the as-built state should be done with consideration of the type of environment.

Work has been done on *in situ* alloying commercially pure Ti with Mo by DED processing but doing this using Ti-6Al-4V was done for the first time in this work, even though the effect seems to be similar to that of the previous work done with commercially pure Ti and Mo.

This research also investigated a commercial β -Ti alloy (Ti-3Al-8V-6Cr-4Zr-4Mo) not previously investigated for additive manufacturing. This alloy gave promising results as a competitive replacement for Ti-6Al-4V, especially in the building of large parts.

6.4 Future work

- More detailed corrosion tests should be carried out in the form of electrochemical measurements and polarization tests to further study the corrosion behaviour of as-built Ti-6Al-4V+10 wt% Mo.
- For the DED samples, further studies should be done to investigate the amount of Mo needed to fully stabilize the β phase, and the presence of ω phase should be confirmed by TEM.
- Anisotropic properties must be studied in more detail. Mechanical testing in this study was in just one direction.
- Other beta stabilizers. This study only looked at 10% Mo. What about another beta stabilizer? Or a combination of 2 or more beta stabilizers such as the commercial alloy. Although I think the problem of unmelted particles will remain even with other beta stabilizers.
- Do actual standardised fracture toughness testing
- Build bigger and more complex components with the commercial beta alloy to see if it delaminates or cracks
- Gas atomize other commercial beta alloy compositions and compare high speed high power SLM with the commercial beta alloy from this study
- Try to get some QuesTalloy powder and do high speed high power SLM. It is claimed to be better suited for SLM than conventional Ti-6Al-4V, but will it also be better at the high speed and high power that AeroswiftTM uses?

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APPENDIX A

The table is the galvanic series of metals in sea water from Army Missile Command Report RS-TR-67-11, "Practical Galvanic Series."

The Galvanic Table

Most Active (Anodic)

- | | |
|--|---------------------------------------|
| 1. Magnesium | 24. Al 2014-0 |
| 2. Mg alloy AZ-31B | 25. Al 2024-T4 |
| 3. Mg alloy HK-31A | 26. Al 5052-H16 |
| 4. Zinc (hot-dip, die cast, or plated) | 27. Tin (plated) |
| 5. Beryllium (hot pressed) | 28. Stainless steel 430 (active) |
| 6. Al 7072 clad on 7075 | 29. Lead |
| 7. Al 2014-T3 | 30. Steel 1010 |
| 8. Al 1160-H14 | 31. Iron (cast) |
| 9. Al 7079-T6 | 32. Stainless steel 410 (active) |
| 10. Cadmium (plated) | 33. Copper (plated, cast, or wrought) |
| 11. Uranium | 34. Nickel (plated) |
| 12. Al 218 (die cast) | 35. Chromium (Plated) |
| 13. Al 5052-0 | 36. Tantalum |
| 14. Al 5052-H12 | 37. AM350 (active) |
| 15. Al 5456-0, H353 | 38. Stainless steel 310 (active) |
| 16. Al 5052-H32 | 39. Stainless steel 301 (active) |
| 17. Al 1100-0 | 40. Stainless steel 304 (active) |
| 18. Al 3003-H25 | 41. Stainless steel 430 (active) |
| 19. Al 6061-T6 | 42. Stainless steel 410 (active) |
| 20. Al A360 (die cast) | 43. Stainless steel 17-7PH (active) |
| 21. Al 7075-T6 | 44. Tungsten |
| 22. Al 6061-0 | 45. Niobium (columbium) 1% Zr |
| 23. Indium | 46. Brass, Yellow, 268 |

- | | |
|--------------------------------------|---|
| 47. Uranium 8% Mo. | 73. Stainless steel 321 (passive) |
| 48. Brass, Naval, 464 | 74. Stainless steel 201 (passive) |
| 49. Yellow Brass | 75. Stainless steel 286 (passive) |
| 50. Muntz Metal 280 | 76. Stainless steel 316L (passive) |
| 51. Brass (plated) | 77. AM355 (active) |
| 52. Nickel-silver (18% Ni) | 78. Stainless steel 202 (passive) |
| 53. Stainless steel 316L (active) | 79. Carpenter 20 (passive) |
| 54. Bronze 220 | 80. AM355 (passive) |
| 55. Copper 110 | 81. A286 (passive) |
| 56. Red Brass | 82. Titanium 5Al, 2.5 Sn |
| 57. Stainless steel 347 (active) | 83. Titanium 13V, 11Cr, 3Al
(annealed) |
| 58. Molybdenum, Commercial pure | 84. Titanium 6Al, 4V (solution treated
and aged) |
| 59. Copper-nickel 715 | 85. Titanium 6Al, 4V (anneal) |
| 60. Admiralty brass | 86. Titanium 8Mn |
| 61. Stainless steel 202 (active) | 87. Titanium 13V, 11Cr 3Al (solution
treated and aged) |
| 62. Bronze, Phosphor 534 (B-1) | 88. Titanium 75A |
| 63. Monel 400 | 89. AM350 (passive) |
| 64. Stainless steel 201 (active) | 90. Silver |
| 65. Carpenter 20 (active) | 91. Gold |
| 66. Stainless steel 321 (active) | 92. Graphite |
| 67. Stainless steel 316 (active) | |
| 68. Stainless steel 309 (active) | |
| 69. Stainless steel 17-7PH (passive) | |
| 70. Silicone Bronze 655 | |
| 71. Stainless steel 304 (passive) | |
| 72. Stainless steel 301 (passive) | |

**End - Noble (Less Active,
Cathodic)**