Ti6Al4V and Expanded Graphite composite material for additive manufacturing via Selective Laser Melting

Grant Daniel Barnsley

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Ti6Al4V and Expanded Graphite composite material for additive manufacturing via Selective Laser Melting

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Supervisors:
Dr Stephen Beirne & Professor Peter C. Innis

This thesis is presented as part of the requirement for the conferral of the degree:

Masters of Philosophy

This research has been conducted with the support of the Australian Government Research Training Program Scholarship

University of Wollongong
ARC Centre of Excellence for Electromaterials Science

March 2019
Abstract

This Masters thesis investigates the development of a tool set that opens new opportunities in additive manufacturing (AM) of metallic composite materials and presents strategies towards its application in selective laser melting (SLM). This was achieved by the modification of commercially available metal powders via a ball milling approach and subsequent modification of an existing SLM system to enhance the capabilities to work with small research quantities of the experimental powders that would otherwise be impractical to deploy in a standard SLM system. Both the composite powder and printed samples have been characterised to understand how the material properties are affected. As this Masters thesis focused upon the challenges associated with development of new SLM methodologies and the development of the underpinning processes and characterisation techniques, only a single ratio of composite material was studied within the time frame scope of this project. The materials selected were; Ti6Al4V, a common commercially available SLM material and expanded graphite (EG). Expanded graphite was added to the titanium base material at a loading of 3% w/w. The 3% ratio was selected as prior work suggested that loadings of 3% for carbon-based additives such as EG can result in measurable differences in the resultant composite material properties.

Due to the nature of the batch ball milling process utilised to produce EG coated Ti6Al4V powder only limited volumes of materials (220g) were produced. Ti6Al4V powder with a median 25-30µm diameter was ball milled in the presence of EG to deposit a consistent coating onto the surface of the Ti6Al4V particles, approximately 300-430nm in thickness. The mechanical interaction from ball milling titanium particles with the EG was noted to alter the nature of the carbon present due to re-compaction of the EG to a more graphitic like carbon. In order to utilise the limited powder supply, extensive modifications were made to the Realizer SLM50 and included; the development of a reduced build volume chamber, re-coater design modifications to accommodate the reduced build volume, and a customised powder hopper. These modifications made it possible to produce meaningful sample structures with as little as 40cm$^3$ of powder and resulted in a bespoke one-of-a-kind SLM system design, suitable for the efficient research and development of new print media.

3D printed geometries were chosen to allow for multiple tests to be conducted on the same sample due to limited powder availability. Analysis of the printed 3D composite structures demonstrated that the EG carbon had significantly, and detrimentally, impacted upon the mechanical properties when compared to samples produced only with unmodified Ti6Al4V. Typically the SLM technique is known to produce more brittle structures as a result of the rapid cooling microstructures that arise as a consequence of the fabrication technique. In order to elucidate the cause for this effect a number of different analysis techniques such as EDS, EBSD, SEM, XRD, Raman, reflectance, density and electrochemical measurements were used to characterise the samples. Here it was found that during the SLM laser welding process carbon diffused into the titanium to form titanium carbide, well known to be brittle and non-ductile. The presence of the TiC and the resultant dendritic morphology formed within the alloyed structure lead to reduction in the mechanical properties of the printed samples. Although the printed architectures were highly brittle with poor loadbearing capabilities, the printed structures retained sufficient integrity that they could be utilised in non-load bearing applications such as porous electrode structures in REDOX based devices.
Surface analysis of the printed composites proved that EG also survived the printing process, with limited conversion into TiC, and was present on all surfaces of the printed samples investigated. The presence of graphitic carbon at the surface was studied to determine if the carbon was electrochemically accessible. Here it was demonstrated that the presence of carbon enhanced the performance of the electrodes in a repeatable manner, enhancing the oxygen evolution reaction (OER) with a reduction in the onset potential. Additionally, the presence of the EG introduced a significant capacitance charging ability typical of electroactive carbon and not observable in unmodified Ti6Al4V structures. These positive effects suggest that the material produced via this approach may be useful in future applications such as water splitting and REDOX based processes.
Acknowledgements

Technical, Academic, Professional and Personal, I’ve had so many forms of support and each one has helped shape this body of work into what it is now. To fully acknowledge all the support I’ve received would be too extensive so I would like to highlight a few key people.

Firstly to my parents Glenn and Maureen Barnsley, you have believed and supported me for all my life and that has given me motivation to go do the things that are important to me. While Glenn may no longer be here, he gave me the motivation that I needed to get my thesis finished. I did not achieve that task in time however, regardless I know both of you are so proud of me for seeing this through to the end.

Renee you have been the love of my life, and whether it was the darkest of days or the brightest, you always brightened up my life. You provided me the strength and motivation to keep facing up to the challenges to see this through, for that I will forever be grateful.

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While this endeavour may not have had the philosophical outcome as originally intended I still think that being a Master at something is still pretty powerful in its own way.

So long and thank you for all the memories.
Certification

I, Grant Daniel Barnsley declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree Masters of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Grant Daniel Barnsley
22nd March 2019
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tr>
<td>ADAM</td>
<td>Atomic Diffusion Additive Manufacturing</td>
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<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BCC</td>
<td>Body Centred Cubic</td>
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<tr>
<td>BMD</td>
<td>Bound Metal Deposition</td>
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<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
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<tr>
<td>CAM</td>
<td>Computer Aided Manufacture</td>
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<tr>
<td>CFF</td>
<td>Continuous Fiber Fabrication</td>
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<tr>
<td>CNC</td>
<td>Computer Numerical Control</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
<td>DED</td>
<td>Directed Energy Deposition</td>
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<tr>
<td>DMLS</td>
<td>Direct Metal Laser Sintering</td>
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<tr>
<td>DMLM</td>
<td>Direct Metal Laser Melting</td>
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<tr>
<td>EBAM</td>
<td>Electron Beam Additive Manufacturing</td>
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<tr>
<td>EBM</td>
<td>Electron Beam Melting</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscatter Diffraction</td>
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<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>EG</td>
<td>Expanded Graphite</td>
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<tr>
<td>EEG</td>
<td>Electroencephalogram</td>
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<tr>
<td>FDM</td>
<td>Fused Deposition Modelling</td>
</tr>
<tr>
<td>FFF</td>
<td>Fused Filament Fabrication</td>
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<tr>
<td>FGM</td>
<td>Functionally Graded Material</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal Close Packed</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
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<tr>
<td>LENS</td>
<td>Laser Engineered Net Shaping</td>
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<tr>
<td>LOM</td>
<td>Laminated Object Manufacturing</td>
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<tr>
<td>LS</td>
<td>Laser Sintering</td>
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<tr>
<td>MMC</td>
<td>Metal Matrix Composite</td>
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<tr>
<td>Nd:YAG</td>
<td>Neodymium-doped Yttrium Aluminium Garnet</td>
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<tr>
<td>OER</td>
<td>Oxygen Evolution Reaction</td>
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<tr>
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<td>Powder Bed Fusion</td>
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<tr>
<td>PDF</td>
<td>Powder Diffraction Files</td>
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<tr>
<td>RPD</td>
<td>Rapid Plasma Deposition</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SLA</td>
<td>Stereolithography Apparatus</td>
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<tr>
<td>SLM</td>
<td>Selective Laser Melting</td>
</tr>
<tr>
<td>SLS</td>
<td>Selective Laser Sintering</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>ASTM Grade 5 Titanium Alloy, 6% Al, 4% V, 90% Ti</td>
</tr>
<tr>
<td>Ti6Al4V-3EG</td>
<td>Ti Grade 5 Alloy with 3% by weight Expanded Graphite Coating</td>
</tr>
<tr>
<td>TRGO</td>
<td>Thermally Reduced Graphene Oxide</td>
</tr>
<tr>
<td>UAM</td>
<td>Ultrasonic Additive Manufacturing</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Powder Diffraction</td>
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1. Introduction

Composite materials are defined as the combination of two or more base materials, classically referred to as a reinforcement and matrix material, [1] with inherently different physical and chemical properties. The need for this classification of materials has been borne out of the need to overcome shortcomings in a particular material and enhance critical properties, such as strength, corrosion resistance, or wear resistance, when being specified for use in an application. This is a well-established practice with common examples such as fibreglass and carbon fibre, where successive layers of the base fibre and textile material are laminated within resins to increase overall strength, while also having the added benefit of a resin surface that can undergo further finishing.

It is this same logic, the addition of filler materials to improve a base materials performance, now being applied to Additive Manufacturing (AM). When AM was first developed in 1984, by Charles Hull, [2] it started by using photocurable resins, such as acrylates or epoxies. Over time it was discovered that by using a combination of these two materials, it is possible to overcome the negative side effects of each. The approach of using multiple materials within AM processes has become increasingly popular due to the demand to fill the material property gaps in the available printable materials. Properties most commonly targeted are mechanical properties such as tensile strength, impact strength and stiffness, however as this expansion is ongoing other material properties such as magnetism, electrical conductivity and thermal conductivity are now being targeted. Filling these material gaps has been an influential driving force for both machine development and materials development. This however, has been a recent growth area in FDM and material jetting technologies with a number of new composite printers hitting the market including: Markforged Continuous Fibre Fabrication (CFF) (Nylon and Fibre), [3] Stratasys Polyjet (up to 6 photocurable resins) [4] and Desktop Metal (“binder” and Metal).[5] Currently, there is no commercially available composite material or printer for Selective Laser Melting (SLM) processes.

Since the start of metal use in AM, there has been a rapid expansion to cover six of the seven primary printing methodologies. Additionally, there has been significant diversity in the printing methods available as well as a broader selection of materials available for manufacturing. In the 1990’s the majority of the methods involved sintering of metals, a technique that has recently been used to create low cost metal FDM systems retailing from $100, 000 USD. [3, 5] Recent expansions to the material market have brought a range of options including: copper-based alloys, tool steels, titanium alloys and carbides. Since 2014 there has been a significant rise in the research for SLM composite metals, most of which have focused on the potential for increase in mechanical or fatigue properties. This increase of composite research is due to the same reason traditional composites were made, to overcome the shortcomings of two materials and make a composite that combines and improves on each material to provide new unique properties not previously available.
However, metals have other material properties that provide benefits to alternative areas of research, such as conductivity and chemical reactivity which can provide useful characteristics for applications in electrochemistry. There is potential to further develop these materials specifically for electrochemical applications and exploit the control over material properties and geometry to produce high surface area novel electrode structures. Materials such as Graphene have been shown in other AM processes to have significant potential as a component of composite materials and is known to provide enhanced electrochemical reactivity and can be functionalised with additional chemicals to further compliment these characteristics.

This body of work aims to cover the overall process required to create composite materials with SLM and evaluate their feasibility for novel electrode structures. It will start by looking at the creation of a composite powder and evaluation of formation processes such as mixing, coating and mechanically alloying to select an appropriate methodology. Additionally, it will cover taking the composite material and processing the powders in an SLM printer to create composite structures. From these structures, investigations will be made looking into the material properties and their potential applications into electrochemical research.

1.1. Additive Manufacturing

Additive Manufacturing as defined by ASTM F2792-12a [6].

"Is any process that can take materials and form them into objects based on 3D model data, this is usually done in a layer by layer process."

The origin of AM is generally attributed to Charles Hull who lodged a patent in 1984 titled “Apparatus for production of three-dimensional objects by stereolithography” [7]. Since the invention of stereolithography, a diverse range of AM methodologies have been developed and commercialised. These methodologies are now organised under seven primary categories. Table 1.1 provides an overview of the commercially available AM processes and indicates if the machines within these categories can to date process metals, composites or both, this does not consider research grade devices and materials. An important distinction within these categories for composite processes and materials must be made: a composite process is where multiple materials are deposited during the fabrication stages and a composite material is where the materials are combined prior to the fabrication stage.

Table 1.1 – Summary of Commercial AM processes identifying Metal or Composite material compatibility

<table>
<thead>
<tr>
<th>AM Methodology</th>
<th>Metals</th>
<th>Composite Processes</th>
<th>Composite Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vat Photopolymerization</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Binder Jetting</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Directed Energy Deposition</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Material Extrusion</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Material Jetting</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Powder Bed Fusion</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sheet Lamination</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>
1.2. Composites

A composite material is a material made from two or more significantly different constituent materials that, when combined, produce a material with measurably different characteristics than the individual materials. [1]. There are five different filler material classes (Figure 1.1A) which can be combined with a base material to result in the five different composite structure types shown in Figure 1.1B. A composite that uses a metal as the matrix is referred to as a Metal Matrix Composite (MMC). It is possible for an MMC to have multiple classes; if it is mixed with ceramics or organics then it is a cermet and if it has three or more materials then it is defined as a hybrid composite. Due to the layer by layer construction manner of AM, it is theoretically possible to adapt processes to alternate build materials over repeated layers and create laminar type composites. This approach is amenable to some AM families more than others and is starting to be commercially realised over a number of the AM categories at a range of print resolutions. Typically, increases in the complexity of materials being processed through AM technologies is leading to higher equipment and materials costs in comparison to simpler, single material print technologies.

By these composite class definitions, there are several semi-established and emergent AM technologies commercially available that utilise a composite approach, including Markforged, Desktop Metal, ExOne and Stratasys Polyjet. This is an area of significant interest in the AM field and it is currently undergoing rapid expansion to be able to achieve previously unavailable material properties.

![Figure 1.1 – Graphical overview of composite materials forms and structures: A) Physical forms of filler materials, B) Common structural arrangement of composite materials - adapted from [1]](image)

1.3. History of Metal AM

Since the invention of additive manufacture in 1984 there has been enormous expansion in the range of printable materials available such as epoxies, acrylates, thermosoftening plastics, ceramics, and metals with new materials being reviewed and introduced on a regular basis. It was not until 1996 that the first commercial machines that were capable of producing metal components, developed by DTM Corp, were released onto the market called Rapid Steel. [2]
Metals can be processed in a variety of ways. Table 1.2 provides an overview of currently available metal printer manufacturers. The number of manufacturers selling powder bed fusion machines reflects that this process has become the most common for producing metal parts. For processing metal parts there are two distinct methodologies of manufacture: sintering and melting. Early printing systems used variations of the sintering type methodology where the basic premise was to bind the metallic particles together before further post processing in a high temperature oven, with one method using a powder mix that incorporated binder and metal. [2] The binder would have a low melting point and cause the metal particles to stick together in the desired shape when heated with a laser. From here the component would be put into an oven and the binder burnt off, and the metal particles sintered together. At this point a porous part has been made, then a low melting point metal, commonly bronze or copper, gets melted down and fills the rest of the structure to achieve a complete metal component. The current alternative now allows directly melting the metal in the desired pattern to progressively build up the part. Due to the direct melting of the powder higher densities are achieved with no sintering process required.

**Table 1.2 – Subset of current Metal 3D printer manufacturers classified by corresponding AM process category**

<table>
<thead>
<tr>
<th>AM Process</th>
<th>Sub Categories</th>
<th>Manufactures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder Jetting</td>
<td>Laser Based Welding (LENS, DMD, LDT)</td>
<td>ExOne, Desktop Metal, Digital Metal</td>
</tr>
<tr>
<td>Directed Energy Deposition</td>
<td>Plasma/Arc Welding (RPD)</td>
<td>Optomec, DMG Mori, DM3D, RPM Innovations</td>
</tr>
<tr>
<td></td>
<td>Electron Beam Welding (EBAM)</td>
<td>Norsk Titanium, Sciaky</td>
</tr>
<tr>
<td>Material Extrusion</td>
<td>FDM</td>
<td>Markforged, Desktop Metal</td>
</tr>
<tr>
<td>Material Jetting</td>
<td>XJet, Vader Systems</td>
<td></td>
</tr>
<tr>
<td>Powder Bed Fusion</td>
<td>Laser Based Welding (DMLS, DMLM, SLM)</td>
<td>DMG Mori (Realizer), SLM Solutions, Concept Laser, Renishaw, EOS, 3D Systems</td>
</tr>
<tr>
<td></td>
<td>Electron Beam Welding (EBM)</td>
<td>Arcam</td>
</tr>
<tr>
<td>Sheet Lamination</td>
<td>UAM</td>
<td>Fabrisonic</td>
</tr>
</tbody>
</table>
The newest methods to become commercially available are utilising sintering and these operate using one of two primary mechanisms: fused deposition modelling (FDM) with a filament with high metal to binder ratio [3, 5] or a binder jetting approach, jetting binder down onto a metal powder. [5, 8] Regardless of which approach is used, the binder is there to hold the form until it can be sintered and burnt off in post-processing. These new systems are trying to fill the need for lower cost metal machines without the need for lasers or inert atmospheres and currently it is being spearheaded by two companies: Desktop Metal using Bound Metal Deposition (BMD) and Markforged with Atomic Diffusion Additive Manufacturing (ADAM).

1.4. AM Build Features

For each AM process the features that are built can change slightly but can be broken down into three main features: Support Structures, Boundaries and Interior (Hatches, Infill). Separating the sections of a print allows for a significant increase in printing control and separate processing parameters can be applied for each section to allow for a better optimised design. There are numerous types of support structures, which change depending on the AM methodology being used, and the software used as some systems can accommodate external processing while others require software from the manufacturer. The function of support structure is to provide mechanical reinforcement and allow easy removal of component from the build tray. Typically angles over 45° from the horizontal can be printed without support, however as illustrated in Figure 1.2B the stereolithography (SLA) process by default preferentially still wanted support on a 45° Section where Figure 1.2A and C didn’t require it. For SLM components this provides two additional advantages: Firstly it secures the part to the build tray to minimise any warping effects that might occur due to excess heat and secondly it provides pathways for heat to be conducted away from the hot weld regions and directs this into the build tray.

![Figure 1.2 – Cross-section of common overhang build geometry depicting typical default support structure arrangements and positioning for A) FDM (uPrint SE, Stratasys) B) SLA (Form 2, Formlabs) C) SLM (SLM50, Realizer [DMG Mori])](attachment:image.png)
Boundaries are primarily separated to achieve higher control over the quality of surface finish and dimensional accuracy. How this is achieved is entirely process dependent however and can result in slowing the speed of material deposition or solidification. The interior region is a complex matter that is also heavily dependent on the AM method used and can commonly be broken down into either infill which is more commonly attributed to FDM components or hatching which is predominant in laser-based processes. Infill is where the interior of a solid body is not filled completely and instead material is deposited in varying patterns and the spacing of these patterns can control the relative density of the Infill. Hatching however solidifies the entire interior region of a part, which is a complex area for laser based processes as heat management is important. If excessive heat is input into parts this will cause distortions and print failures, however if insufficient energy is used then properties such as density and strength will start to suffer. A comparison of Infill and Hatching is shown in Figure 1.3, comparing an FDM processed region to an SLA method, the laser passes for the hatching on the SLA are such that the entire layer will solidify where the FDM process will result in triangular hollow cavities. As more AM methods move towards voxel processing some manufacturers are allowing each voxel region to have different processing conditions and practically for laser-based processes this means that components can be heat mapped and energy density increased or decreased depending on expected heat levels to prevent excessive build-up of heat.

![Figure 1.3 – Single layer for a rectangular cross-section showing Boundary and Infill Configuration](image)

A) FDM (Mark Two, Markforged) B) SLA (Form 2, Formlabs)
1.5. AM Processes

While metal AM may have started purely with Powder Bed Fusion (PBF) processes, it is now available in most AM methodologies with a very diverse range of materials. An overview here will be presented on each of these methods focusing on how metal or composites are being processed in each case.

1.5.1. Material Extrusion

Material Extrusion systems are currently the most prevalent systems on the market and are the primary form of printer used by non-commercial consumers. The most common of these systems known as Fused Deposition Modelling (FDM) or Fused Filament Fabrication (FFF) machines work by taking a thermosoftening polymer filament feed stock and feeding it into a liquefier chamber [2]. In this chamber, heat is applied to melt the material, so it can then be extruded out of a nozzle. As the material is extruded it solidifies into the intended design pattern, typically using 2D layers, and stacks these layers until the component is completed (Figure 1.4). A number of companies have developed a range of metal filaments (<50 wt% Metal) that are compatible with most FDM systems including Bronze, Copper, Aluminium, Steel and Magnetic Iron, that are made up of dispersed metal particles within a polymer matrix. [9, 10] Another example of a composite filament is the carbon fibre loaded nylon material marketed by Markforged, made up of approximately 25 wt% carbon fibre within a nylon matrix. Additionally, this can be further combined into another composite structure by placing fibres within a plastic matrix, known as continuous fibre fabrication (CFF), illustrated in Figure 1.5.

![Figure 1.4 – Schematic representation of the operation of fused deposition modelling (FDM) or free form fabrication (FFF) extrusion based systems - adapted from [11]](image-url)
With the release of FDM machines capable of processing full metal parts, the concept of heating and softening the material remains, but now with a metal particle composite filament which has a high concentration of metal particles added with small amounts of binder, as the binder melts it facilitates the flow to occur. In the case of Desktop Metal, a secondary extruder is employed to create a thin layer of binder at the interface between the model and support. This binder layer is later removed as the parts are sintered together allowing the part to easily be removed from the support structures. This composite build process is depicted in Figure 1.6. As the binder is burnt off parts undergo approximately a 10% shrinkage, as this occurs the metal particles start sintering and final part densities are in excess of 95%.
1.5.2. Material Jetting

Material jetting covers processes where all the material is deposited via inkjet print heads. This process has three major aspects: material, droplet deposition and material curing, with the overall process shown in Figure 1.7. Compatible materials must be a liquid or a particle solution that can undergo an evaporation or crosslinking process to allow solidification. It is important to note, however, that not all liquids are printable. Printability depends on a number of variables some of which are material dependent (particulates, density, viscosity) and some are machine dependent (velocity and nozzle diameters). Research has been done in this area to develop a printing index that offers an indication of the likelihood that a specific sample will print. [2] Droplet deposition follows the same principles found in ink jet printers and utilises some of the same technologies. Through this fabrication method it is possible to control each droplet and create matrices using more than one type of material, primarily resins which can be jetted and then cured with ultra-violet light. This level of droplet control is utilised within machines such as the J750/J735 from Stratysys where it has six different model materials, and over 360,000 different droplet combinations are possible. This large number of combinations of materials means that it is incredibly versatile for creating composites and has shown promise in creating high definition medical models with the capability of correctly tailoring the soft tissues and bones. A highly detailed multi-element example print representing the anatomical features of the human shoulders and head is shown in Figure 1.8A.

![Figure 1.7 – Schematic of Photopolymer based Material Jetting System indicating layer-by-layer deposition of UV curable droplets to form 3D structures - adapted from [11]](image)
A recent expansion to this technology is from XJet. This proprietary method uses Nano particulate solutions to allow printing of metals and ceramics. The Nano particulate suspension allows the material to be jetted out of the print head. As the droplet is deposited it is heated at 300°C to cause the liquids to evaporate leaving only the deposited metal particles. Once printing is finished the parts still have to be sintered to fuse the metal or ceramic particles together for their full-strength capabilities. In terms of resolution, the Xjet has a layer thickness of under 2 microns [14] as compared to the 14 microns quoted for flagship Polyjet printers from Stratasys. [4]

1.5.3. Binder Jetting

Binder jetting was developed during the early 1990’s. The process at the time was called “3D Printing” and was largely pioneered by ZCorp. [15] The process for this AM method involves depositing a binder down on to a powder substrate, whether it be a polymer, metal or ceramic. This methodology is intrinsically adaptable to most materials on the provision that the correct powder size can be achieved and an appropriate binder to adhere particles together is selected. The process of how the binder is applied is very similar to traditional ink jet printers and in the case of companies like ZCorp they used available standard HP print heads [16, 17] to minimise cost. This process can easily incorporate colours into the binder or jet binder and colour separately, making it one of the first multi-coloured AM processes. For this process there are two main stages of the build: powder application and binder application. Powder application involves depositing fresh powder and then levelling it, commonly using wiper arms or blades. The jetting system incorporates jetting a matrix of small droplets over the intended cross-sectional area which will bond the deposited binder particles together and stick the fresh layer on to the previous layer. Once printed, these composite powder/binder parts are typically very brittle and will require post processing to enhance the strength. A useful feature about this process is that it does not require support structures as the parts are supported by the surrounding
powder. Two such examples of metal printer binder jetting machines include ExOne, who supply a wide variety of machines aimed at production, prototyping and research and already have a diverse material catalogue including steels, Inconel Alloys and Tungsten carbide. [8] Secondly is Desktop Metals production series machine which is being aimed at a mass production market as it has a substantial cm³/hr throughput of material compared to other metal alternatives. [5] In either case parts have to be post processed to sinter the metal particles together and burn off the binder agents. This print process is illustrated in Figure 1.9.

![Figure 1.9 – Schematic of the binder jetting process where binder solutions are selectively added while spreading layers of porous powders. Non-bound powder acts as structural support media - adapted from [2]](image)

### 1.5.4. Directed Energy Deposition

Directed Energy Deposition (DED) systems work by melting material as it is deposited onto a substrate, with the earliest systems developed in 1997 by Optomec with their Laser Engineered Net Shaping (LENS) technology. [2] This system can be used with any material that is capable of melting and can be in either wire or powder form. In the case of metal powders, the process involves the controlled spraying of a powder and then using a laser to target the stream of powder, resulting in a point in the stream where molten material is being formed, which can then be controllably deposited over the build area. Alternatively, if a metal wire feed system is used, an arc welding system similar to traditional MIG welding is utilised. [18] The construction method of parts is very similar to that of extrusion based systems in that it forms deposition pathways and builds on top of them. It is not uncommon however for these machines to have multi axis heads that can reduce the amount of support structures required for parts. An area that utilises this technique is repairs, in particular for metal parts that have had sections of material damaged and removed as regions can be built back up and processed for corrections. Newer methods such as seen in DMG Mori’s Lasertec range of
machines utilise this DED approach with 3D Hybrid variations available, combining with traditional machining to be able to achieve a machined finish on a complex component in a single process. Figure 1.10 illustrates the basic DED process and how the tracks are layered to create the shape.

Figure 1.10 – Schematic of a typical laser powder DED process where powder particles are fed into the path of a focused laser source to induce melting and fusion with layers below - adapted from [2]

1.5.5. Sheet Lamination Process

Sheet lamination process involves taking flat material from a roll or sheets, which can be composed of paper, plastics or metals. These sheets are then layered and bonded together. This bonding can be performed in a number of ways, with the most common being heat and glues to bond the layers. If glue is used in this process a laminated composite structure is created [1]. The layers can be cut around the perimeter before or after bonding depending on the process, using either a knife or a laser with the rest of the material cross-hatched, allowing for easy post removal access. While this process was one of the first commercialised in 1991 [2] it is not an overly common methodology used amongst the present market of AM. One of the current manufacturers of a metal lamination process is Fabrisonic who use an ultrasonic additive manufacturing (UAM) approach which involves depositing metal foils and then ultrasonically welding the foils together to achieve a near net shape. [20] Fabrisonic also couple this mechanism with a CNC milling approach to remove the excess foil and achieve the desired final geometry and surface finish. A typical Laminated Object Manufacturing (LOM) setup is shown in Figure 1.11.
1.5.6. Powder Bed Fusion

Powder Bed Fusion (PBF) processes utilise a build platform that is coated by a fine layer of powder prior to regions being selectively fused together, which is generally performed by lasers. Powder bed fusion has a large range of acronyms including: Selective Laser Sintering (SLS), Laser Sintering (LS), Direct Metal Laser Sintering (DMLS), Direct Metal Laser Melting (DMLM), and Selective Laser Melting (SLM). LS is considered a generic term and can be applied to nearly all different approaches of powder bed fusion. It should be noted that for most current applications the sintering in the acronyms are presently more of a misnomer due to machine and process improvements with full or partial melting now the more common mechanism. SLS is used primarily for plastics, while DMLS, DMLM and SLM are primarily used with metals. A number of these acronyms are used because specific companies have patented certain technologies including: recoating mechanism, software and laser scanning strategies and are therefore more of an indication of brand of manufacture than a distinction of methods. Further specialisations exist because the energy required to melt plastics and metals are vastly different and therefore the chemical reactions that can occur depending on the surrounding atmosphere can have varying effects on the processes as well. Generally, using argon is preferred for inert atmospheres as it has a lower likelihood of reacting with the metals during welding. A basic schematic of the system can be seen in Figure 1.12 which shows a basic SLS system in which the major components comprise of a roller (leveeller), build platform and laser.
Another variant of this technology is Electron Beam Melting (EBM) shown in Figure 1.13, which instead of using a laser to initiate melting uses an electron beam to melt the powder. A benefit over the other metal PBF processes is that due to presence of a vacuum it can print at higher temperatures and with more reactive materials. This processing method helps protect the material and slow cooling rates resulting in better grain structures without post processing. This difference in grain structure is why EBM is highly valued in the aerospace industry as the “As printed” components are regarded as having better mechanical properties, primarily due to improved ductility due to the grain structures having achieved larger grains and/or equilibrium phases.
1.6. Selective Laser Melting

Selective Laser Melting (SLM) is a powder bed fusion technique developed to melt fine metallic powder using lasers. The underpinning technology for SLM process came out of the Fraunhofer Institute for Laser Technology (ILT) during the 1990’s, [22] with the first patents lodged in 1997. It was not until 1999 however, that this research was able to be successfully commercialised by F&S Stereolithographietechnik GmbH, which in 2009 split to form SLM Solutions AG and Realizer GmbH. [22] The machine that will be used for this thesis is a Realizer SLM50, an open access platform that facilitates operating parameter modification, and as such ideal for low volume materials research and process development.

1.6.1. SLM Process

The three major components of any SLM are: a recoating unit, a laser and a build platform. The specific recoating mechanism varies between all the different manufacturers but is typically a strip of silicone housed in a metal frame that will drag the powder across the build tray in either a linear or a rotational motion. The laser is typically a Nd:YAG laser at a wavelength of 1064nm with a typical power range of 0.1-1kW. Lastly the build platform will typically come in two shapes either circular or rectangular with rounded edges to improve the sealing surfaces. There will be numerous other machine differences that will effect potential applications and useability, however they will not interfere with the basic operating mechanism. The arrangement as used in the Realizer SLM50 that is used for this body of work is depicted in in Figure 1.14. The basic process can be summarised into three major steps:

1. Recoating unit deposits and spreads a fine layer of powder over the build platform.
2. The laser rasters a pattern over the powder, melting the particles together.
3. The build platform lowers ready for the next layer application.

![Schematic of Realizer SLM50 Setup adapted from [23]](image)

**Figure 1.14** – Schematic of Realizer SLM50 Setup adapted from [23]

### 1.6.2. SLM Process Parameters

The SLM process is complex and controlling the laser and in turn the weld formation has a number of influential variables involved. The control parameters for SLM all focus on affecting the energy density transferred into the material to initiate the weld. Figure 1.15A shows the basic process overview for a single layer, this comprises of two primary features: the hatch and the boundary. Both the hatch and the boundary are made up of overlapping weld lines, with each line made up of multiple laser exposures, Figure 1.15B shows how these layers are then stacked in alternating direction to help minimise porosity. Table 1.3 identifies and describes the most common print parameters that are controlled for the SLM50, the three most important control parameters for affecting energy density are: Laser Intensity, Point Distance and Exposure Time. Point distance and exposure time are only relevant for systems that turn the laser on and off between mirror repositioning. Some systems instead use continuous laser scanning and the relevant parameter is scanning speed. Alternatively some manufacturers may choose to simplify user control by combining the two variables to form a scanning speed approximation. The energy density from the laser can be estimated by Equation 1.1 [24] with scanning velocity (v) able to be approximated by the point distance divided by the exposure time.

\[ E = \frac{P}{vdh} = \frac{P}{\frac{P}{t}dh} \]  

**Equation 1.1**
Table 1.3 – Realizer SLM50 Control Parameters

<table>
<thead>
<tr>
<th>Control Parameter</th>
<th>Description</th>
<th>Units</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Intensity</td>
<td>Power output from the laser (max 100W)</td>
<td>W</td>
<td>P</td>
</tr>
<tr>
<td>Point Distance</td>
<td>Distance between each laser exposure point</td>
<td>µm</td>
<td>p_d</td>
</tr>
<tr>
<td>Exposure Time</td>
<td>The time that the laser stays on to dwell on a point</td>
<td>µs</td>
<td>t</td>
</tr>
<tr>
<td>Hatch Spacing</td>
<td>The distance between each scan line</td>
<td>µm</td>
<td>h</td>
</tr>
<tr>
<td>Layer Thickness</td>
<td>How thick a layer of material is deposited</td>
<td>µm</td>
<td>d</td>
</tr>
<tr>
<td>Build Platform Temp</td>
<td>The temperature that the build platform is heated to (max 200°C)</td>
<td>°C</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.15 – SLM Processing Strategy A) Individual scan layer B) Stacked alternating layers, adapted from [23]

Figure 1.16 illustrates the basic principles of how varying these parameters can affect the weld pool region, if the exposure time or intensity is increased the weld pool formed will be larger, if the point distance is increased too much then the weld pools will not form a continuous weld track. The practical results for what the weld tracks look like are shown in Figure 1.17. Figure 1.17B represents what would be considered a reasonably normal weld, which will typically exhibit lower spatter and higher consistency of the weld width. The balling effect (Figure 1.17A) and the over welding (Figure 1.17C) are a result of insufficient or excessive energy densities occurring during the weld process. Typically, when optimising parameters, a trade-off is required between the desired goals, whether it is optimised for density, accuracy, speed or more commonly finding a median result across all categories.
Figure 1.16 – SLM Processing Effects on Weld Regions – Visual representation of potential weld pool size differences as a function of operating parameter settings

Figure 1.17 – Characteristic Single Weld Track Formation Types: A) Balling B) Normal C) Over Welding D) Excessive Speed adapted from [25]
Figure 1.18 – Cross-section of a SLM Weld Profile and Characteristics

Figure 1.18 shows how the hatch spacing and weld width relate to each other. Hatch spacing is related to weld width with the constraint that it must be less than the weld width to minimise porosity. This is not a variable that is commonly used to adjust the energy density as it is normally adjusted for after varying the Laser Intensity, Point Distance and Exposure Time to find a stable weld region and the weld width. These settings can then be used to influence the hatch spacing. There is control over the layer thickness, however the minimum value of this parameter is usually dictated by the median particle size of the powder being used. Lastly, while the build platform temperature can be adjusted to both decrease the temperature differential required to weld and to lessen the cooling rate this parameter for titanium is set at the highest possible setting which for the SLM50 is 200°C. The cooling rate is important as the faster the welds cool the finer the microstructure that is created in the metal and the finer the microstructure typically the more brittle the sample becomes. [26] However in the case of SLM printed components the brittleness is additionally affected due to the non-equilibrium microstructure which occurs due to the rapid cooling rates. Figure 1.19 shows the weld structures of an Inconel printed sample, Figure 1.19A can be seen to be comparable to Figure 1.15A with the consistent hatch spacing and scan direction visible. Further Figure 1.18 is seen to be represented by Figure 1.19B with the Gaussian energy distribution visible forming the weld penetration shape and a repeated hatch spacing.
1.6.3. Hatching

Hatching involves applying the parameters discussed in 1.6.2 strategically to achieve optimal results in the final produced components. For SLM these parameters can be applied independently onto the Boundary, Support and Hatching to achieve desired effects. Boundaries are the perimeters of the shape and can either be internal or external perimeters. Typically, with SLM these are generally one weld width but can be controlled if additional welds are desired and can impact greatly on features such as surface roughness and dimensional accuracy. An example of how the boundary is generated is shown in Figure 1.20, with the original model contour shown and an offset from the boundary has been done to allow for the weld width, which will result in an increase in the dimensional accuracy and can be tailored to suit the processing parameters.

Hatches can be seen in Figure 1.21. This processing will result in a high-density internal volume. Hatches typically have a higher energy density than boundaries and supports to achieve minimal porosity within the sample. Due to this higher energy density, if the right scan strategies are not employed it may result in a build-up of heat within the part and result in possible deformation or failure. [28] Scan strategies can break the layer into smaller regions and randomly process to better manage the heat build-up, which is further improved upon if coupled with remelting processing. Remelting is where areas are welded multiple times to ensure that there is minimal porosity within
the part, and can be broken into pre-hatch, hatch and fill lines. Pre-hatch is where there is enough energy input to sinter/partially weld the powder, which is followed by hatch where it will fully melt the metal. Lastly on areas that are prone to porosity such as the boundary-hatch interface additional fill lines can be added to better fuse these regions together resulting in a higher density component.

For Realizer Software there is one further feature that can be utilised and is referred to as a point structure. A point structure is a complex 3D lattice that is based upon a defined repeat unit, with each layer made up of individual laser points generating separate weld regions, rather than the overlapping weld regions that are used for the other features. For each subsequent layer of the point structure the positions of the points are moved such that the weld region generated on the new layer will still grow to a size to merge with the point from the previous layer. These structures are of particular interest for their potential to be used in novel porous electrode structures. An illustrated example of a BCC repeat unit is shown in Figure 1.22A, in the real samples the weld pools are much closer together and have larger overlaps creating a more cylindrical shape. Similar features can be formed by other methods and different manufacturers may have similar design features however this method is unique in that the size of the beams when made out of titanium are approximately 100-150µm in diameter (Figure 1.22B) a feature size not achievable on other commercial systems except for the SLM50.
1.6.4. Materials

SLM can theoretically use any weldable metal as long as it can be processed into the correct size and morphology and a sufficiently powerful laser is available. A primary restriction on the materials for SLM is that the material has to be manufactured to have the correct particle size which for SLM machines is commonly in the order of 20-35µm [28]. Most metals can be pre-processed to have a specified particle size; however, there are a limited number of methods by which the morphology of the particles can be made spherical, which is preferred for SLM. Spherical particles are preferred but not essential as they provide an enhanced flow characteristic allowing uniformity of the recoating for each layer of material over the build volume. The most common method for spherical particle production is gas atomisation, where liquid metal is forced through a nozzle and blasted with high pressure gas [29] as shown in Figure 1.23. The angle and pressure that the gas hits the molten metal stream will heavily affect particle size and sphericity. Each machine will have specific requirements for material and as a basic rule the higher the resolution, the finer the particle sizing needs to be. For example, Realizer recommends for the SLM50 to use particles no greater than 63µm with the recommended powders typically having a median size of 20-30µm.
1.7. SLM Composites

The research into composite materials for use in SLM has been increasing significantly in recent years as the technology has matured and become a more popular method of part production. SLM is showing significant uptake in the aerospace and medical industries due to its ability to create high strength complex geometry components [30, 31], and as a result has been a primary focus area for research, even expanding into composite methods. [30, 31]

1.7.1. Currently Tested Composites

The number of publications focusing on composite development for use with SLM has shown significant growth with Figure 1.24 showing the number of publications that are showing keywords SLM, Composite and AM. Not all composite work has specifically been intent on creating composites with modified material properties with one of the oldest articles found the composite nature of the material was only brushed over as it was deemed of lesser importance. [32] This trending increase in research is illustrating the diverse potential of composites, not only limited to SLM, but the broader Additive Manufacturing community.
Table 1.4 summarises 33 composites to offer an overview of the materials and methods used to create the composite materials. The primary materials used are mainly restricted to common SLM materials including Steels, Aluminium Alloys, Inconel’s and Titanium alloys. This is understandable as most researchers have used available on hand materials already in appropriate format for use with their respective SLM machines. The secondary materials are a more diverse selection and have specifically been chosen depending on the targeted goals attempting to be achieved in the structures, but common applications include biomedical [33-36], hardness/wear resistance [37-41] and high strength [42-47]. Amongst all of these materials a range of methodologies are applied to create the composite powders, including: ball milling, high energy ball milling, mixtures, electrostatic assembly, chemical vapour deposition (CVD) and gas atomisation.

<table>
<thead>
<tr>
<th>Primary Material</th>
<th>Secondary Material(s)</th>
<th>Manufacture Method</th>
<th>Date of Publication</th>
<th>Authors</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>nHA</td>
<td>Ball Mill</td>
<td>2015</td>
<td>Q. Wei, S. Li, C. Han, et al</td>
<td>[34]</td>
</tr>
<tr>
<td>316L</td>
<td>TiB₂</td>
<td>Mixture/High Energy Ball Mill</td>
<td>2017</td>
<td>B. AlMangour, D. Grzesiak, J. M. Yang,</td>
<td>[37]</td>
</tr>
<tr>
<td>Al</td>
<td>Al₂O₃</td>
<td>High Energy Ball Mill</td>
<td>2017</td>
<td>Q. Q. Han, R. Setchi, et al</td>
<td>[43]</td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td>Mixture</td>
<td>2017</td>
<td>N. Kang, P. Coddet, J. Wang, et al</td>
<td>[40]</td>
</tr>
</tbody>
</table>

Figure 1.24 – Annual number of publications on SLM composites between 2010 and 2018 based on Web of Science Core Collection and Keywords: additive manufacturing, Selective Laser Melting and Composite
<table>
<thead>
<tr>
<th>Material</th>
<th>Additions</th>
<th>Method</th>
<th>Year</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi10Mg</td>
<td>AlN</td>
<td>Ball Mill</td>
<td>2015</td>
<td>D. Dai, D. Gu</td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>Al₂O₃</td>
<td>Ball Mill</td>
<td>2017</td>
<td>J. B. Jue, D. D. Gu</td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>Carbon Nanotube</td>
<td>Ball Mill</td>
<td>2015</td>
<td>X. Zhao, B. Song, W. Fan, et al</td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>TiB₂</td>
<td>Gas Atomisation</td>
<td>2017</td>
<td>X. P. Li, G. Ji, J. P. Kruth, et al</td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>TiC</td>
<td>High Energy Ball Mill</td>
<td>2014</td>
<td>H. Wang, D. Gu</td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>TiC</td>
<td>High Energy Ball Mill</td>
<td>2015</td>
<td>C. Ma, D. Gu, D. Dai, et al</td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>WC</td>
<td>Electrostatic Assembly</td>
<td>2017</td>
<td>J. H. Martin, B. D. Yahata, J. M. Hundley, et al</td>
</tr>
<tr>
<td>Boron Carbide (B₄C)</td>
<td>Cobalt (Co₂B)</td>
<td>CVD</td>
<td>2015</td>
<td>A. Davydova, A. Domashenkov, et al</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>CuSn, CuP</td>
<td>Mixture</td>
<td>2007</td>
<td>D. Gu, Y. Shen</td>
</tr>
<tr>
<td>Fe</td>
<td>SiC</td>
<td>Mixture</td>
<td>2013</td>
<td>B. Song, S. Dong, C. Coddet</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>304L</td>
<td>In-situ Mixing (FGM)</td>
<td>2016</td>
<td>B. E. Carroll, R. A. Otis, et al</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>MWCNT</td>
<td>Mixture (Dispersion and Evaporate)</td>
<td>2016</td>
<td>P. Wang, B. C. Zhang, et al</td>
</tr>
<tr>
<td>Ti</td>
<td>HA</td>
<td>Unknown</td>
<td>2018</td>
<td>C. J. Han, Y. Li, Q. Wang, et al</td>
</tr>
<tr>
<td>Ti</td>
<td>Ta</td>
<td>Mixture</td>
<td>2015</td>
<td>S. Sing, W. Yeong, F. Wiria</td>
</tr>
<tr>
<td>Ti</td>
<td>TiB₂</td>
<td>Ball Mill</td>
<td>2014</td>
<td>H. Attar, M. Bonisch, et al</td>
</tr>
<tr>
<td>Ti</td>
<td>TiC</td>
<td>Ball Mill</td>
<td>2017</td>
<td>B. B. He, K. Chang, et al</td>
</tr>
</tbody>
</table>
1.7.2. Structures of Composite Powders

As previously mentioned there are numerous published methods for introducing multiple materials to create a composite powder for printing. The three most common production mechanisms used are: pure, coated and mixed, as demonstrated in Figure 1.25.

![Figure 1.25 – Composite Material Mechanisms A) Pure: raw material component mixtures B) Coated: thin coating of secondary material onto primary C) Mixed: Secondary material impregnated within primary material](image)

**Pure**: Is where each component used to create the material is introduced without alteration. This is specifically limited to a mixing approach and are prone to material segregation due to dissimilarity in particle size or density. [35, 40] While papers have identified segregation as undesirable they have not acknowledge if this has affected the final results. [57, 62]

**Coated**: Is where a secondary material is coated onto a primary material. This has been published as being performed by low energy ball milling [33, 34], CVD [41] and electrostatic assembly. [42] This method will primarily maintain the particle shape of the primary material and is typically used for low ratios of nanoparticles to base powder coatings.

**Mixed**: Is where the secondary material is forced into the primary and is mainly performed by high energy ball milling. This can be used for high ratios and larger particle sizes; however, this destroys the original particle morphology and reforms it, reducing the flow characteristics typically. [39, 43]
Table 1.5 – Methods and Mechanisms for Production of Composite Powders

<table>
<thead>
<tr>
<th>Method</th>
<th>Mechanism</th>
<th>Materials that can be used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing</td>
<td>Pure</td>
<td>Ideal for materials of similar density and morphology otherwise segregation will occur. Particle size would prefer on the smaller size to ensure that the right ratio is typically in laser spot. Otherwise distinct weld regions will occur.</td>
</tr>
<tr>
<td>Low Energy Ball milling</td>
<td>Coating</td>
<td>Best used with two materials that are significantly different density or size difference to encourage coating</td>
</tr>
<tr>
<td>CVD</td>
<td>Coating</td>
<td>When the coating required involves a liquid or a controlled deposition thickness</td>
</tr>
<tr>
<td>Electrostatic Assembly</td>
<td>Coating</td>
<td>Used to bind nanoparticles onto gas atomized powders</td>
</tr>
<tr>
<td>Solution Coating</td>
<td>Coating</td>
<td>Using a liquid dispersion to coat the solid particles and evaporating liquid after coating.</td>
</tr>
<tr>
<td>High Energy Ball Milling</td>
<td>Mixed</td>
<td>Best done with metals as this ends up crushing and deforming to create a mixing action</td>
</tr>
<tr>
<td>Gas Atomization</td>
<td>Mixed/Alloying</td>
<td>An alloy base is formed prior to gas atomization, may either form mixed particles or alloyed homogenous particles.</td>
</tr>
</tbody>
</table>

1.7.3. Ball Milling

Ball milling can be applied in two distinctive means to create composite powders: coating or mixing materials together. Typically coating two materials together requires one to be in an already suitable state for use with SLM, while the second material is typically much smaller in size. [34, 45, 59, 60] The smaller particle used in current research has been on the nano scale, which has resulted in low weight ratio composites. For coating purposes low energy ball mills are used with typical running times less than 10 hours, which has been shown to be sufficient to bind a coating onto the larger particles. [45, 59, 60] This method minimises the damage to the larger particles and as a result the composites should present flow characteristics similar to the original primary material.

When mixing is desired this method requires high energy ball mills and is typically described as mechanical alloying, also requiring longer running times typically in excess of 20 hours. This is ideal when the secondary materials are either metals or not on a Nano scale. [49, 50, 56] In this process, as the materials start to bind, the larger primary particles will flatten and cold weld together, and eventually fracture into smaller components. This process is outlined in Figure 1.26. Once these particles are fractured the morphology is very rough and far from ideal. Allowing further processing time enables the particles to be partially smoothed into a form that should be suitable for SLM. This method has successfully been used to introduce graphite into a Ti and Al matrix for the purpose of creating in situ TiAl alloy and reinforced with TiC deposits which are sub 1µm in size. It was noted that while the intent was to form TiAl and TiC the final results formed TiAl₃, Ti₃AlC₂ and TiCₓ. While this contained the elemental groups desired, energetic reactions between the titanium and carbon made it difficult to have complete control over the alloying process. [49]
Figure 1.26 – Fracture Mechanics of Producing Composite Material Powder via Mechanical Alloying (Ball Milling) through addition of Titanium Carbide to a common grade of gas atomised Aluminium Alloy powder - adapted from [49]

These ball milling methods are the most common approaches that are utilised in current research methods. The choice about which method is to be used comes down to the materials that are desired in the compound, and both methods will result in different particle morphology characteristics which will affect the flow ability of the final samples. One drawback of ball milling is that the particle size of the material will decrease so it is important to start with materials larger than what the system requires. [49] Another drawback of high energy ball milling is the reduced sphericity due to the fracturing of the particles present.

1.7.4. Multi Material Mixing

Mixing powders can be a viable option depending on the available materials with convection type mixing being the most common, particularly for solid-solid mixtures. Convection type mixing involves putting both desired materials together and agitating the powders in a repetitive manner until they are evenly distributed. [63] With solid-solid mixtures however a common problem depending on the flow and size characteristics of the particles is that segregation of the mixture can occur. Segregation is an undesirable characteristic as this will lead to inconsistent results if this is to be subsequently used in SLM machines. Segregation can be avoided at the mixing stage if the correct selection of mixer is made, however upon material handling segregation may start to occur. A recommended mixer flowchart is shown in Figure 1.27. It can be seen that if segregation issues exist the following types of mixers might be suitable for use: tumbler, orbiting screw and ribbon mixers. Alternatively, if segregation persists consider re-selecting materials of similar size and density or attempting an alternative composite manufacturing technique.
With regards to processing mixed powders it is important to remember the fundamental mechanisms of the SLM process which is to melt the powder in a controlled manner. [32, 51, 57] The desired results will influence the operating parameters required depending on which material is targeted to be melted. If there are two materials that will melt, settings that target the lowest melting point would result in encapsulation of the other material. [57] Alternatively if the high melting point is targeted then both materials would melt. Currently there are no available studies that explore this mechanism and how it impacts on the printed components, specifically if there would be distinct melted regions for each material or if it would include small alloyed sections.

Mixtures can also be created using Solid-Liquid methods. While the mixers stay similar, the major difference is that the liquid phase is evaporated and then the material is tumbled to return it to a free flowing state. Solid-Liquid mixture methods are ideal in getting smaller particle sizes to bond onto the larger metallic powders and prevent segregation occurring. [47, 53] Notably this has been successfully used to introduce carbon in the form of multi wall carbon Nano tubes (MWCNT) [47] which showed degradation during the printing process and graphene nanoplatelets [53] which remained in the printed samples.

1.7.5. Alternative Methods

Three alternative methods used specifically for SLM have only a single published source as proof of concepts and hold potential for further investigations and include: CVD [41], Electrostatic Assembly [42] and Gas Atomisation. [40] Chemical Vapour Deposition is an established means for cladding powders and has been popular amongst many industries for applying a coating layer onto a powder material. [41] It is possible to have the metallic component of these powders be the base coating or the cladded material. Depending on whether the metal component of the powder is in the cladding or in the centre is likely to affect the achievable results but as of yet no current detailed analysis has been done showing its use in SLM. One of the few studies has however shown the feasibility of ceramic-metal composites [41]. Figure 1.28 is an example of the powder produced, with the thin 2µm layer of cobalt allowing the melting and binding of particles together when forming structures.
Another method of preparing powders that has been proven to be effective is electrostatic assembly. This method uses charge manipulation to control the attraction between the materials and cause them to assemble, and by changing the amount of charge in the system, the ratio of materials can also be controlled. [64] In the case of SLM materials this concept was paired with crystal lattice structure matching, to make sure that when the particles assembled they did so in a controllable and repeatable manner. [42] This method was used to create five different composite materials, shown in Figure 1.29.

Figure 1.29 – Nanoparticle assembly on AM powders: A) AL7075 powder with TiB₂ nanoparticles, B) Ti6Al4V powder with ZrH₂ nanoparticles, C) Al7075 powder with WC nanoparticles, D) AlSi10Mg powder with WC nanoparticles and E) Iron powder with TiC nanoparticles adapted from [42]
The final method that has shown promise at creating composite materials is Gas Atomisation. This method is the same as what is used to create standard SLM powders and was previously discussed in Section 1.6.4. Gas atomisation first involves creating the master alloy which is to be atomised, in this instance TiB$_2$ was mixed with molten Al to form an initial alloy and in a secondary stage is mixed in with molten AlSi10Mg. [40] After the final alloy is produced it is run through the gas atomiser as per standard operating techniques to produce the desired particle sizes. This process represents the most feasible technique for SLM companies to implement in future materials as it utilises the same process in which the standard base materials are formed, however it has the highest cost factor to implement which will inhibit the uptake of users. Samples of the composite powder are shown in Figure 1.30.

![Figure 1.30 – SEM Images of AlSi10Mg with nano-TiB$_2$ powder: A) Morphology, B) Surface, C) cross-section, D) TEM bright fielded image [46]](image)

1.7.6. Functionally Graded Materials

Functionally graded materials have been produced using a range of metals most commonly focusing on hardness or strength modification. The main reason for interest in graded materials is the ability to delivery targeted material properties to a specific region, allowing better material optimisation of design, this targeted delivery is only practical at present through AM processes. [52] These materials have had limited research in relation to metals due to the complexity of trying to deposit multiple materials controllably. Mostly the research has been done on DED machines as they can have a combination of wire and powder or multiple powder feeds allowing a ratio to be changed between the different material feeds, allowing for a larger gradient change over the structure. [52, 62, 65-68] Notably via this methodology studies have been done in varying the Ti6Al4V to TiC ratio to have control over the hardness of the product and as a result develop defined regions of increased wear.
resistance. Limited research has been done using PBF techniques, with the main method in these approaches being to stop mid print to remove a material and introduce a new one, meaning that the gradient has only occurred over a few layers before being purely the secondary material. 

It is important to note that in DED only the material that is deposited is lost, whereas with the PBF technique the second material introduced will be permanently contaminated and unrecoverable, and this limits its practicality.

1.8. Metallurgy

For this body of work the metallurgy analysis will be limited to an overview of titanium compositions and the basic effects of the alpha and beta alloying elements, how SLM affects the microstructure, and highlight the possibilities that may occur for an interaction between titanium and carbon. This information is important because for metals it only takes minor changes in composition and processing parameters to significantly change the final material properties of the produced components.

1.8.1. Titanium Alloys

The classification of Ti alloys is based on the main phase present in the alloy at room temperature, which is affected by the elemental composition. At room temperature, pure unalloyed titanium has an HCP structure, and this is referred to as the α phase. Titanium is an allotropic material and when it exceeds the β transition temperature (approximately 882°C) it reforms into a BCC structure. By alloying titanium it is possible to affect the volume fraction of the α and β phases at room temperature. The alloying elements may increase or decrease the α/β transition temperature or provide solid solution straighteners and not affect the transition temperature. Table 1.6 shows common α and β stabilisers and in the case of Ti6Al4V, both α and β stabilisers have been added into the alloy. The Vanadium present in Ti6Al4V is responsible for decreasing the beta transition temperature and therefore at room temperature this alloy consists of both α and β phases.

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Approximate Range, wt%</th>
<th>Effect on Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>2-7%</td>
<td>Alpha Stabilizer</td>
</tr>
<tr>
<td>Tin</td>
<td>2-6%</td>
<td>Alpha Stabilizer</td>
</tr>
<tr>
<td>Vanadium</td>
<td>2-20%</td>
<td>Beta Stabilizer</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2-20%</td>
<td>Beta Stabilizer</td>
</tr>
<tr>
<td>Chromium</td>
<td>2-12%</td>
<td>Beta Stabilizer</td>
</tr>
<tr>
<td>Copper</td>
<td>2-6%</td>
<td>Beta Stabilizer</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2-8%</td>
<td>Alpha &amp; Beta Strengthener</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.2-1%</td>
<td>Improves Creep Resistance</td>
</tr>
</tbody>
</table>

With Titanium α and β alloys there are three primary types of microstructures seen: Lamellar, Bimodal and Equiaxed. Lamellar are made up of longer thin needle like crystals forming grains, while equiaxed is more characterised by grains and crystals that have approximately equally dimensioned x and y axes. A bimodal microstructure is a mixture of both Lamellar and Equiaxed structures. These three microstructure arrangements are depicted in Figure 1.31, although the scale bars are not consistent across the images of the three states, distinct differences in their structure is clear. Grain
sizes and what microstructure is achieved is highly dependent on rate of heating and cooling and the processing conditions over the β transition temperature. [26] Figure 1.32 shows some examples of the diversity of microstructures that are achievable, each one of these microstructures have been analysed as the mechanical properties vary and this can be used to tailor the mechanical properties to the desired application. The microstructure heavily influences a number of the mechanical properties achievable in the titanium alloys, however typical trends observed are higher rates of cooling lead to finer grain structures and this typically leads to increased tensile strength at the cost of ductility to the point where the material can become brittle. [26, 73]

![Figure 1.31 – Typical Ti6Al4V Microstructures A) Lamellar, B) Bimodal, C) Equiaxed [73]](image)

![Figure 1.32 – Heating and cooling rate effects on Microstructure for Ti6Al4V [26]](image)
The range of available titanium alloys is quite diverse depending on the desired application, with typical applications utilising properties of high strength-to-weight ratio, corrosion resistance and/or low thermal expansion co-efficient. [74] Most alloying components are selected due to the effects they have on the alpha and beta characteristics. The various ASTM grades of Titanium exist due to trying to improve the mechanical/material properties for different applications or processing techniques. An example of this is the addition of 0.04-0.08% palladium which is typically undertaken where enhanced corrosion resistance is required. Grade five titanium is normally referred to as Ti6Al4V and is the most common alloy due to its balance of material properties, weld-ability and heat treatability, allowing it to be utilised everywhere from aerospace to medical implants.

1.8.2. SLM Printing Effects on Titanium

SLM samples as printed inherently have a different microstructure than traditionally formed Ti6Al4V components, however through heat treatments it is possible to make the microstructure comparable. This similarity can be seen by comparing microstructures in Figure 1.32 which is from a Titanium billet specialist to SLM sample microstructures achieved by heat treatment shown in Figure 1.34C-H. SLM inherently has a large cooling rate due to high temperature differentials, resulting in fine Lamellar grains as shown in Figure 1.31A [73]. What is distinctive for SLM is that due to interlayer weld penetration, the grains grow in the direction of the build (Z-Axis) and have fine elongated grains, an example of which is shown in Figure 1.33A and B. These fine grain structures typically lead to high strength [75] however result in brittle structures until heat treatment is performed to refine the grain structures. Figure 1.34A and B shows the microstructures of printed samples and demonstrate how the three different heat treatments (Figure 1.34C-H) can result in different grain structures similar to those discussed in Section 1.8.1. The effect of the microstructure will be an important consideration when analysing printed samples especially since as adding secondary materials for composites will change the alloying phases present in the microstructure.

![Figure 1.33 – SLM Ti6Al4V grain growth characteristics A) Side View sample 1 B) Side View sample 2 C) Scan Parameters Applied to sample 1 D) Scan Parameters Applied to sample 2][76]
Figure 1.34 – Optical and SEM of heat treated SLM Ti6Al4V samples, A-B) As Printed, C-D) 835°C/1.5h/AC, E-F) 905°C/1.5h/AC, g-h) 975°C/1.5h/AC [75]
1.8.3. Carbon and Titanium Compounds

Titanium and carbon have only one common compound that they will form which is Titanium Carbide (TiC). TiC is notably an extremely hard ceramic and is primarily used in surface modifications for tools to form hard cutting edges or wear resistant surfaces. [62] Depending on the processing conditions different sub-stoichiometric ratios of TiC\(_x\) can be formed. [39] When these reactions are occurring in-situ these sub-stoichiometric ratios are a result of fast cooling rates that limit the diffusing of carbon into the TiC crystal lattice. [39] TiC formation is likely to occur if both materials are present and has been seen to occur in SLM processing [39] and ball milling. [77] TiC has been used in composite research for SLM primarily with the intent of modifying material properties such as hardness, strength and wear characteristics. [39, 49, 50, 54, 59-61]

1.9. AM in Electrochemistry

AM is seeing significant penetration into most fields of scientific research whether it is for creating jigs and fixtures allowing for more repeatable experiments or direct applications of complex geometries and materials. The basic motivations as to why this is occurring is the same basic incentive for any potential application field and can be simplified to four primary reasons these being rapid prototyping, geometric complexity, customisation and decreased waste this is shown summarised in Figure 1.35. Electrochemistry is one such area currently seeing some of these applications, with research directed into three primary areas [78]: Sensing, Energy and Synthesis. Each area is using and applying AM in different ways to capitalise on the relevant strengths for the respective projects.

![Figure 1.35 - Advantages of 3D printing as compared to traditional manufacturing methods adapted from [79]](image-url)

There is a lot of overlap as to how each of the different applications for electrochemistry are utilising the capabilities of AM. Some of the most common reasons include enhanced surface area, coatings and increased functionality and can be seen depicted in Figure 1.36. Surface area enhancement can
be performed a number of ways starting with basic increases in surface area due to geometric control. Further to this the component can be modified with features like nanotubes or chemically dealloying the material to create porosity at the surface. Depositing coatings on the geometry can be done a number of ways, the intent is to bind a more reactive material onto a substrate to be able to do a further chemical reaction. Increased functionality extends to being able to condense multi component features down into a single device, for example implanting a gas distributor within a complex lattice electrode. As this field of research is developing the researchers are creating ever more complex and intricate ways to incorporate the advantages of AM into the electrochemistry applications.

**Enhance surface area**

- Printed porous structure
- Surface patterning

**Enhance surface porosity**

3D printed microstructure (µm resolution) → nanostructuring → Modified 3D printed microstructure (nm features)

**Dealloying**

**Enhance electrode functionalities**

- 3D printed structure
- raw material + active component
- 3D printing

**Gas diffusion channels**

- Deposited active component
- 3D printed structure with active component
- conductive ink

*Figure 1.36 - Common Post-processing of 3D-Printed Electromaterials Employed for Electocatalysis [79]*
1.9.1. Sensing

Sensing covers any detection or measurement technologies, including electrodes for signal detection such as electroencephalogram (EEG) [85] and microfluidic devices for detection of particular compounds. [86, 87] For the EEG electrodes, base structures are fabricated from FDM devices and then silver and gold coatings are applied for conductive and corrosion resistance. There is a growing number of papers of microfluidic devices utilising AM however at present most of the electrodes are still the traditionally fabricated ones with the AM used aimed at the flow cells. The material jetting method is an increasingly popular choice for microfluidic device creation due to its resolution, for example the J750 from Stratasys has 20-85µm XY resolution and 14µm Z axis resolution [4] which puts it on a scale to be able to utilise capillary flow effects important to microfluidics. Some of these microfluidic devices are being combined with microneedles to allow for the sample collection, [88-91] which can be produced on 2 photon polymerisation which is one of the highest resolution printing methods, although is significantly limited by its build volume.

1.9.2. Energy-related Applications

Energy has a wide range of applications for AM, as it is allowing for production of high surface area electrodes and complex geometry. These attributes allow for research into some interesting fields such as interdigitated supercapacitors, which may be directly fabricated out of a desired material or coated after the fabrication of the structure. [92] In energy areas, it is important that the structures are conductive and have high surface areas. While metal is popular, graphitic compounds such as Graphene Oxide (GO) [93] and Thermally Reduced Graphene Oxide (TRGO) have shown significant promise as functional additives used in novel electrode fabrication. [94, 95]

1.9.3. Synthetic Processes and Electro-synthesis

While AM use in creating electrochemistry-based synthetic reactors is still in its early stages it is showing significant promise in allowing for bespoke chemical reactors for applications such as water splitting [81, 96] and microfluidic reactionware. [97-99] Similar to the energy related applications benefiting from the high surface area which is increasing the number of reaction sites, synthesis is using this to enhance the chemical reactions occurring at the electrodes allowing for such applications as water splitting. As for the microfluidic approach it is primarily benefiting from having controlled mixing and diffusion of products within a device, [97-99] with geometry able to be tailored for multiple reactions to occur within the one microfluidic chip. [98]

1.9.4. Applications for SLM

SLM at present is more uniquely suited to energy and synthetic processes because it allows for direct fabrication of metal structures which can tailor unique geometry and high surface areas. The range of materials and the increasing research into composites is uniquely positioned to greatly benefit both of these areas, whether it be for a highly conducting material such as copper or silver to allow high electron transfer rates or for nickels chemical composition for water splitting applications. With ongoing research into the hardware for SLM technologies such as 400W 515nm wavelength lasers for copper printing, the expanding range of materials at present shows no sign of slowing down. [100] Composite research into SLM materials has shown significant increase in activity since 2014 and has focused on a variety of areas, most commonly for strength as it allows for unique fine tuning of
material properties to achieve enhanced performance results. It is this same concept that will be taken and applied in this body of work but with an intent for applications in electrochemistry.

1.10. Objectives

This work has a number of important objectives, namely to:

1) Development of methodology to produce a composite material comprising of Ti6Al4V powder from TLS Technik GMBH and 3wt% EG, while maintaining a powdered feedstock appropriate for use with SLM.
2) Improve the capabilities of the SLM50 to work with small research volumes of experimental material so as to conserve the limited amounts of print media.
3) To produce 3D printed samples suitable for structural, mechanical and electrochemical analysis; and to characterise these and the feedstock powder in order to understand how the addition of carbon into the print media effects the printing process.

1.11. Thesis Outline

The remaining chapters are arranged as follows; Chapter two looks at the experimental procedures and methodologies that will be utilised in this study; Chapter three will analyse the composite powder produced and how it degrades over production cycling, as well as comment on how this may affect printed structures and repeatability. Chapter four will analyse the printed composite structures and how the material composition has affected the material properties, while also overviewing the potential for novel electrode structures. Lastly, Chapter 5 offers a concise insight into the data interpretation and outlines where future research could take this project further.

2. Characterisation Methods

As outlined in the literature review there is many possibilities in composite materials for SLM to be able to better tailor the material properties to suit specific applications. This chapter focuses on the equipment used to perform the analysis and the methodologies used with each relevant process, presented in sufficient detail such that replication of results on similar systems should be feasible. All the pieces of equipment used followed the standard operating procedures for the relevant systems and the recommended analysis methods if available.

2.1. Reflectance Measurements

Reflectance is an important characteristic for laser-based printing methods such as SLM as the light is imparting energy on the powder and this energy is then comprised of two components. One component goes to heating up the powder to melt it and the other part is what is reflected and is essentially lost energy. By quantifying the reflectance value of a material, it can therefore offer an indication of how much of the energy will be transferred to the powder to initiate the welding process. The reflectance can have significant impact on the printability of materials, which is why materials such as copper, silver and gold are so challenging to print with as they have reflectance values typically exceeding 70%. Most SLM machines including the SLM50 utilise a 1064nm (Nd:YAG) laser. With the Shimadzu UV3600 Spectrophotometer (Figure 2.1) it is possible to analyse the reflectance at the 1064nm range and determine approximately how much light will be reflected
from the powder and therefore not absorbed by the material. The settings used to capture the data on reflectance are shown in Table 2.1.

![Shimadzu UV3600 used for Reflectance Measurements](image)

**Figure 2.1** – Shimadzu UV3600 used for Reflectance Measurements

<table>
<thead>
<tr>
<th>Settings for Shimadzu</th>
<th>Integrating Sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration</strong></td>
<td>Reflectance</td>
</tr>
<tr>
<td><strong>Selected Parameters</strong></td>
<td>External 2D</td>
</tr>
<tr>
<td></td>
<td>Slit Width 5.0</td>
</tr>
<tr>
<td><strong>Wavelength Range</strong></td>
<td>800-1200nm</td>
</tr>
<tr>
<td><strong>Scan Speed</strong></td>
<td>Medium</td>
</tr>
<tr>
<td><strong>Scan Interval</strong></td>
<td>0.5nm</td>
</tr>
</tbody>
</table>

**Table 2.1** – Shimadzu UV3600 Measurement Configuration for Reflectance of Powders

2.2. **Density**

Measuring the density to determine the porosity of a sample is one of the most common analyses performed on samples produced by SLM. The reasoning for this is that there is a significant link between porosity and mechanical strength, which is normally attributed to pores acting as crack initiators. There are many ways to analysis density and three notable ones that can be used for the types of samples produced are Archimedes, Optical Analysis and Micro CT. However, the Archimedes method, which is the most publicised method, has been deemed too inconsistent to be considered reliable due to the available equipment and sample sizes and therefore is not contained in the density analysis performed in this body of work. MicroCT measurement analysis at present are uncommon due to the expense of the machine and the analysis performed being resource intensive. However,
this measurement method offers some of the highest accuracy for analysing the porosity nature of samples with machines available with resolution down to 50 nm\(^3\) voxels, [101] making it one of the most comprehensive and accurate measurement methods.

### 2.2.1. Optical Analysis

Optical analysis involves taking 2D images of a polished sample and post processing the images to determine the ratio of solid material to pores present and extrapolating this data into the third dimension. The images used have been taken using a Leica DM6000 but due to errors with image stitching in the Leica software each image has to be individually analysed and then averaged for the layer observed. By using scientific image processing software such as ImageJ the voids can be analysed and the total area extracted. This method does have some drawbacks in that there is typically a margin of error because it assumes a consistent porosity across the layers which may not be the case depending on geometry and processing conditions. In order to account for this both the Front and Top planes of a dogbone sample will be analysed and averaged.

The steps involved for analysing included:

1. Original images captured in greyscale (enables simpler thresholding)
2. Threshold the images
3. Filter the images
4. Analyse the porosity

![Figure 2.2](image)

**Figure 2.2 – Optical imaging processing example in which original greyscale image captured via Leica DM6000 (A) is post processed via ImageJ software and user defined filters to isolate dense filled metal region (B) for further quantitative analysis**

Step four is the most important part of the analysis process. By this step the image has been processed to a binary state, in which black is the solid printed sample and white is the background or pores, an example of which is shown in Figure 2.2B. ImageJ software suite can then perform porosity analysis where it subtracts the background component to analyse the pores within a sample, the results of which provides the pixel area for the solid and porous regions. Since porosity is unitless it’s not necessary to correct the pixel\(^2\) to m\(^2\) area, however this scale factor is available within the Leica software suite. The scripts used to process the images output two files: A Particle Summary and Colour Count and are presented in Appendix 1. The particle summary contains the area of the pores present while colour count provides the solid area as a count of number of black pixels, these are combined as shown in Equation 2.1 to determine the percentage of porosity.
2.2.2. MicroCT

CT scanning uses X-Rays creating a series of 2D images rotated around a single axis. By analysing the difference in the X-Ray absorption, it is possible to reconstruct a 3D representation of an object showing the regions of different densities. Micro CT uses these same principles, but the process has been refined for higher resolution, in this case performed with a Bruker SkyScan Micro-CT system with a voxel size of 1µm³ used here. As MicroCT images are taken around an axial centre it is necessary to rebuild the transaxial planes to have the conventional X, Y and Z transaxial planes, as depicted in Figure 2.3. In Figure 2.3 it is possible to observe the most common artefact of this process is the radiating circular lines, which if not corrected will turn up in the reconstructed data. The images are partially processed in Bruker NRecon software, where they are rotated, cropped, binary thresholded and despeckled. From here it is still necessary to process the MicroCT images via a 3D median filter to remove the noise from the ring artefacts. This was conducted within Matlab R2016a with the scripts shown in Appendix 2. The final stage of the processing is through a medical imaging software such as Materialise Mimics, which rebuilds the 2D images into a 3D model. The 3D model consists of two components: the pores and the solid body. From these files a volume analysis of the porous and solid sections can be performed directly. The volumes are then converted to a porosity value using the equation shown in Equation 2.2.

![Figure 2.3 – Reconstructed 2D image of a slice through a Transaxial Plane of a Ti6Al4V dogbone sample captured through MicroCt with a voxel resolution of 1µm](image)

\[
\frac{\text{Porosity Volume}}{\text{Porosity Volume} + \text{Solid Volume}}
\]

Equation 2.2

While this method is probably the most accurate currently available, it does have a number of drawbacks. Firstly it is a time intensive process to image and post process the data, and secondly the machines can only measure a small volume at a time. In the case of the reconstructions used here only a 500µm section from the middle of the dogbone samples were analysed, meaning any variations over the build height are not observed.
2.3. Raman Spectroscopy

Raman spectroscopy is a common method of analysing materials, in particular Carbon as Raman spectroscopy has been established as a valid means of distinguishing between forms of carbon present, for example amorphous, graphite or graphene. Since the secondary material in the composite powder was selected to be the expanded graphite form of carbon this method of analysis was chosen to observe what happens to the carbon throughout the process. Understanding the carbon state is important to be able to determine what useful electrochemistry may be applied to the final printed samples. It is important to note that most carbon bonds will start to degrade around 1000K and with Ti6Al4V having an approximate melting point of 1700K, it is likely that a degradation of the graphite structure will occur. An additional consideration is that Raman uses a localised testing method with the setup used depicted in Figure 2.4 focus down to a 1µm spot size is possible. This allows for accurate results, however if there is any variation in the sample it can lead to a large variation in results and consequently a larger number of sample sizes required to obtain a true depiction of what is occurring. The settings used in the analysis of samples are shown in Table 2.2.

![JY HR 800 Raman Spectroscopy system utilised for Carbon Characterisation](image)

Table 2.2 – JY HR 800 Raman Spectroscopy Measurement Configuration

<table>
<thead>
<tr>
<th>Settings for Raman Spectroscopy</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Laser</strong></td>
<td>632nm</td>
</tr>
<tr>
<td><strong>Lens</strong></td>
<td>MPlan N 100x Objective</td>
</tr>
<tr>
<td><strong>Mapping</strong></td>
<td></td>
</tr>
<tr>
<td>Spacing - 1µm</td>
<td></td>
</tr>
<tr>
<td>Exposure time – 2s</td>
<td></td>
</tr>
<tr>
<td>Accumulation – 3</td>
<td></td>
</tr>
<tr>
<td><strong>Point / Point Mapping</strong></td>
<td></td>
</tr>
<tr>
<td>Exposure time – 5s</td>
<td></td>
</tr>
<tr>
<td>Accumulation – 10</td>
<td></td>
</tr>
</tbody>
</table>
In terms of analysing the Raman Results Figure 2.5 shows an example of the data captured, with carbon on the surface of a printed part being used as a sample. The G Band at 1570cm\(^{-1}\) is a result of in-plane vibrations and represents the SP\(^2\) bonded carbon atoms (for example C=C). The D Band at 1350cm\(^{-1}\) is an indication of the disorder and is the out of plane vibrations, there can also be a secondary D' band at 1620cm\(^{-1}\) which the presence is also an indication of an increase in amount of disorder and defects present. Simply put the G band indicates planar sheets while D band indicates defects. [102] In relation to the types of carbon this can represent it means that graphene which is sheets of carbon atoms exhibits strong G band signals where graphite typically exhibits stronger D band signals as it is randomly packed carbon sheets. The G’ band or commonly referred to as the 2D band depending on sharpness, intensity and presence of a shoulder can provide an indication of the number of layered carbon sheets and is present in both graphite and graphene samples however graphene will exhibit a stronger signal than graphite.

Since the D and G band results are strongly related to the form of carbon present by analysing the D/G ratio an understanding of the type of carbon present and quality can be understood. A ratio closer to zero will be indicative of strong G band signal and therefore be of high quality graphene, whereas a ratio closer to one may be indicative of a graphitic quality and would have to be considered in conjunction with the other data. If the ratio greatly exceeds one, then a strong D band signal is measured and would indicate that the carbon present is no longer in the form of sheets. Diamond is one such form of carbon that exhibits Raman Spectra like this. Considering the D/G ratio of 1.16 observed in Figure 2.5 it would indicate a graphitic type material. Consideration of the G’ peak which exhibits a shoulder it can be inferred that the carbon present is comprised of large stacks of carbon sheets.

Figure 2.5 – Raman Spectroscopy carbon example identifying common peaks caused by SP\(^2\) and SP\(^3\) carbon bonds
2.4. Elemental Composition using Energy-Dispersive X-ray Spectroscopy (EDS)

With a composite material it is important to characterise where and quantify the ratios of each material present. During the powder preparation stage both the titanium powder and the graphite powder was measured to have a 3%wt loading however after handling and transferring containment vessels the final values seen in the powder and printed samples may differ. Energy-Dispersive X-ray Spectroscopy (EDS) is an available means of measuring this variation in loading. EDS works by stimulating emission of x-rays from a sample by firing a beam of charged particles at the surface. As the particles impact the sample, electrons are released from the atoms and this causes X-rays to be emitted with the energy proportional to the electron shell the electron came from. By measuring the energy of the X-rays coming off the sample it is possible to determine elemental composition. This analysis method can be performed simultaneously during SEM imaging to determine the elemental composition. The SEM used in this testing was a JEOL JSM 7001F and is depicted in Figure 2.6, and it was run at a 5keV configuration with the probe current adjusted to 4nA. At 5kV the peaks detected for Ti and V overlap and lack sufficient identifying features that occur in the 5-15kV range, and as a result for this analysis no vanadium results are recorded. The penetration or the interaction volume is important to consider as the results will primarily determine the elemental composition at the surface. As such, for coated particles it would be expected to read a higher proportion of the coating materials as compared to the core materials.

Monte Carlo simulation is an accepted means of approximating the interaction volume and is depicted in Figure 2.7. The electron range can be calculated via the following formula

\[ R_{KO}(\mu m) = \frac{0.0276A}{Z^{0.89}\rho} E_0^{1.67} \]  

Equation 2.3

Where \( A = \text{Atomic weight} \left( \frac{g}{\text{mole}} \right) \), \( Z = \text{Atomic number} \), \( \rho = \text{density} \left( \frac{g}{cm^3} \right) \) and \( E_0 = \text{Electron Beam Energy (keV)} \).
Once the interaction volume is determined the volume equations for hemisphere and partial hemisphere calculations along with the ratio of carbon to titanium in the EDS can be used to determine an approximate thickness of the carbon layer, as depicted in Figure 2.8 as the “h” dimension.

$$V = \frac{2\pi}{3} r^3$$

$$V = \frac{1}{3} \pi h (3r^2 - h^2)$$

2.5. Microstructure analysis via Electron Backscatter Diffraction (EBSD)

For metals, different grain structures and material phases can affect the material properties dramatically. Typically, samples printed by SLM without post processing are very brittle due to rapid cooling resulting in very fine grain structures. The best technique to analyse the crystal structures and in turn acquire information about the grain and phase formations is EBSD. EBSD is used within a SEM and uses backscatter electrons that diffract off the sample. The patterns these electrons generate are
called Kikuchi bands. [105] The pattern offers unique observations of crystal geometry and orientation, and by comparing the detected information to known reference database it is possible to identify the material phase present. With the complexity of the pattern analysis it is common for the operator to specifically select phases of interest for comparison to limit the amount of data captured, therefore it is important to have an approximate understanding of what is expected to be present. If the correct comparison crystal structures are not selected then the material will remain as an unidentified result and will require retesting with a different selection. Using this technique, it is possible to observe the microstructure for the Ti6Al4V samples and then observe the changes that occur with the addition of EG and how this in turn affects further material properties such as hardness and tensile strength. The EBSD is performed on the same equipment used for the EDS depicted in Figure 2.6, with the mapping settings shown in Table 2.3 applied.

<table>
<thead>
<tr>
<th>Table 2.3 – Jeol7001 EBSD mapping configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Settings for EBSD mapping</strong></td>
</tr>
<tr>
<td>Electron Beam Voltage</td>
</tr>
<tr>
<td>Scan Raster</td>
</tr>
<tr>
<td>Step Size</td>
</tr>
<tr>
<td>No. of Points</td>
</tr>
<tr>
<td>Phase Detection</td>
</tr>
</tbody>
</table>

### 2.6. X-ray Powder Diffraction (XRD)

X-ray Powder Diffraction (XRD) is used for phase identification of crystalline material similar to EBSD, but employs techniques similar to EDS. XRD works by bombarding the target material with electrons, as the electrons impact the material they dislodge other electrons. When an electron is knocked out of its respective shell it emits an X-ray, and by measuring and collating this data over a range of sample angles it is possible to determine information about the crystal lattice structure and orientation. [106] Similar to EBSD this data is compared to known references and databases to determine what materials are present. As the comparison methodology is simpler than EBSD it makes XRD ideal for identifying unknown crystalline materials. This method makes it ideal to detect if the titanium and carbon present in the prepared composite materials are combining to form additional compounds. All the XRD measurements were performed using a GBC MMA X-ray generator and diffractometer shown in Figure 2.9 and using the scan parameters in Table 2.4.
2.7. Vickers Hardness Testing

Hardness is an important characterisation tool for metallic samples as it characterises the samples ability to resist plastic deformation. Hardness testing in metals follows a roughly linear trend when compared to the tensile strength however this is not always the case and will depend on the material. The machine used for these tests was a Durascan Struers Micro Indenter utilising a Vickers Hardness method. The machine can be setup and run in an automatic mode reducing the potential for human error which is quite typical of hardness measurements. The recommended Durascan load is dependent on hardness as the ideal indentation size is 60µm diagonals as it allows for use of the highest magnification objective. Excessive force will result in a larger indentation and having to use a lower objective both of which will impact on the accuracy of the measurements.

Vickers hardness is determined by the following equation.
\[ HV = 0.0018544 \times \frac{L \text{ (kgf)}}{d^2 \text{(mm)}^2} \]  

Equation 2.4

Where \( d \) is the average of the two diagonals as depicted in Figure 2.10.

![Indenter (Diamond Pyramid)](image1)

**Figure 2.10 – ISO 6507 Image Extracted for Principles of Vickers Test identifying A) pyramidal indentation geometry B) diagonal measurements used for HV calculations - adapted from [107]**

An array of nine points was conducted on the larger section of the dogbone samples, as shown in Figure 2.11. Loading of 0.5kg were used on the Ti6Al4V samples while the Ti6Al4V+3EG had to be increased to one kilogram loads.

![Sample of Ti6Al4V dogbone printed on SLM50 embedded in resin and polished, used for Vickers Hardness Testing with the numbered grid indicating the nine data points that final HV is averaged over](image2)

**Figure 2.11 – Example of Sample of Ti6Al4V dogbone printed on SLM50 embedded in resin and polished, used for Vickers Hardness Testing with the numbered grid indicating the nine data points that final HV is averaged over**

### 2.8. Electrical Conductivity

For determining the electrical conductivity of a sample commonly there is the two-point probe and the four-point probe methods. The four-point probe is normally considered the more accurate as it takes into consideration the contact resistance with the sample, however this method is more difficult to set up and is better suited to larger simpler samples. In this case the two-point measurement will be used with multiple measurement lengths to determine and account for the contact resistance, which in turn makes it comparable to the accuracy of the four-point probe. When a sample is measured for the resistance there are two components that make this up.

\[ R_{\text{tot}} = R_{\text{Contact}} + R_{\text{Sample}} \]  

Equation 2.5
Resistance of a sample is dependent on length.

\[ R_{Sample} = \frac{\rho l}{A} \quad \text{Equation 2.6} \]

Where \( \rho \) is the resistivity of the sample, since it is length dependent by taking multiple measurements over known lengths the results can be used to determine the contact resistance and solve for \( \rho \).

\[ R_1 = R_{Contact} + \frac{\rho l_1}{A_1} \quad \text{Equation 2.7} \]
\[ R_2 = R_{Contact} + \frac{\rho l_2}{A_2} \quad \text{Equation 2.8} \]

For a simple sample where the cross section remains constant \( A_1 = A_2 \) which allows further simplification of the equation.

\[ R_1 - R_2 = R_{Contact} + \frac{\rho l_1}{A_1} - R_{Contact} - \frac{\rho l_2}{A_2} \quad \text{Equation 2.9} \]

\[ \Delta R = \frac{\rho l_1}{A} - \frac{\rho l_2}{A} \quad \text{Equation 2.10} \]
\[ \Delta R = \frac{\rho}{A} (l_1 - l_2) \quad \text{Equation 2.11} \]
\[ \rho = \frac{\Delta R \times A}{(l_1 - l_2)} \quad \text{Equation 2.12} \]

By repeating this test an averaged sample value can be attained.

### 2.9. Characterisation of Electrodes

Measuring electrode performance can be done in a number of complex ways depending on specific materials and reactions trying to be achieved. However for simple analysis 2 common characteristics have been identified: surface area and catalytic activity of a material. Surface area is important as with a larger area there are more potential sites for reactions to take place. Catalytic activity refers to the rate of reaction, and this, the higher catalytic activity, the faster the reactions. Generally, higher catalytic activity correlates with higher system current, therefore voltammetry measurements can be used to measure performance of electrodes.

#### 2.9.1. Three Electrode Setup

For electrode analysis a three-electrode system is one of the most popular arrangements due to its incorporation of a reference electrode which provides the reference required to control and monitor the system potential. The three components of the electrode set up are: working electrode (electrode being studied), counter (auxiliary) electrode and a reference electrode. The reference electrode has a known voltage potential and allows the potentiostat to correctly determine applied voltage and the current going between the working and counter electrodes. [108] A basic arrangement configuration is shown in Figure 2.12A along with the used arrangement shown in Figure 2.12B. With this setup the
voltage or voltage scan rate is what is applied to the setup and the result being measured is the current that is being generated. The sparge tube allows for the purging of oxygen from the electrode setup which in turn results in cleaner and more accurate results, in this case nitrogen was used for the purge gas. For the reference electrode an Ag/AgCl electrode is used and positioned as close as possible to the working electrode in a 0.1Mol NaSO₄ electrolyte. For the counter electrode the primary criteria is to ensure that it has a larger accessible surface area, so by using the 1.0mm BCC Ti6Al4V electrode it can be ensured that a larger surface area than the 1.2 and 1.4mm BCC electrode structures will always be present. Figure 2.13 shows the as produced electrodes and for use in the three-electrode setup they were prepared as shown in Figure 2.14. The prepared electrodes have wires attached via an M3 bolt and the base area has been insulated using UV curing adhesive to minimise its influence on testing results.

Figure 2.12 – 3 Electrode System Examples A) Indicative idealised setup adapted from [108] B) Final arrangement used utilising a 3D printed nylon composite spacing jig to increase repeatability of electrode positions and a standard glass vial
2.9.2. Voltammetry Setup

An electrocatalyst has two common means of evaluation: apparent total electrode activity and the intrinsic activity of the catalytic sites. The total electrode activity is described by the maximum current density standardised by the surface area (A cm$^{-2}$). The intrinsic activity of a catalytic site is more complex to establish and is better suited for fundamental studies of catalytic activity. Intrinsic activity is normally described by the turnover frequency (s$^{-1}$) and the hardest component to evaluate in this process is the electrocatalytic active surface area. [109] For the purposes of this preliminary study the characterisation has been limited to the total electrode activity to be analysed using cyclic voltammetry. Cyclic voltammetry is a common analysis tool used for basic electrode characterisation and works by measuring the current response of the electrode over a linear ramped voltage range for a repeated number of cycles. The important analysis component of this is to measure the peak current response of the working electrode, as this can indicate either an increase in reaction area available or increase in the reactivity of the material. Cyclic Voltammetry was performed using the settings shown in Table 2.5. From these results cycles 2-5 were averaged, standardised using surface roughness and cropped to the 0V-1.5V range to perform the analysis on.
Table 2.5 – Cyclic Voltammetry Scanning Parameters

<table>
<thead>
<tr>
<th>Voltammetry Setup</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scan Rate</strong></td>
</tr>
<tr>
<td><strong>Voltage Range</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Number of Cycles</strong></td>
</tr>
<tr>
<td><strong>Scan Direction</strong></td>
</tr>
<tr>
<td><strong>Initial Potential (E_i)</strong></td>
</tr>
</tbody>
</table>

2.9.3. Surface Roughness Estimation

Surface area is a basic electrode characteristic due to the correlation between surface area the number of reaction sites present. [109] When different electrode sizes are used it is important to standardise by the surface area as this will allow a more valid comparison between different designs. It can be very hard to determine the surface area of an electrode therefore it is common to estimate the available surface area by considering the electrode as simple geometric shapes and using standard equations for the surface areas. This coarse approximation of surface area however does not accommodate changes in surface roughness that have a significant influence on available surface area. SLM surface roughness is due to the powders used, and as the powder is melted some particles on the boundary can either partially melt or due to sufficient heat, sinter onto the surface of the component, resulting in a significant increase in available surface area. For the purpose of these initial investigates an approximation of the surface area can be made by calculating the flat surface area and then assuming that due to the spherical particles there is a hexagonal packing hemispherical surface finish. Figure 2.15 shows the surface finish of an as printed lattice structure in Ti6Al4V from an SLMS50, and Figure 2.16 shows the proposed hemispherical packing structure. Starting from the basic formulas for area of a circle and surface area of a sphere a resulting scale factor for the ideal geometry can be created.
Figure 2.15 – Surface finish on a ‘as printed’ lattice structure, showing Ti6Al4V powder particles partially welded onto the surface of the structure, Made on Realizer SLM50 from Ti6Al4V sourced from TLS Technik.

Figure 2.16 – Single Layer of Hexagonal Packing Sequence for Spherical Bodies [110]

\[ \frac{SA_{\text{ideal}}}{\pi r^2} \approx \text{No. of Hemispheres Present on Surface} \]  
Equation 2.13

\[ SA_{\text{Rough}} = \text{No. of Hemispheres} \times 0.5 \times 4\pi r^2 \]  
Equation 2.14

\[ SA_{\text{Rough}} = \frac{SA_{\text{ideal}}}{\pi r^2} \times 0.5 \times 4\pi r^2 \]  
Equation 2.15

\[ SA_{\text{Rough}} = 2SA_{\text{ideal}} \]  
Equation 2.16
The final result is Equation 2.16 and from this a simple scaling factor can be applied. It is important to consider that this scaling factor was arrived at independently of the available geometry which means it can be applied to any sample to estimate the surface area. The ideal surface area can either be calculated from basic math equations for simplified geometry or extracted directly from a CAD program if more complex designs are required. For the electrodes used in this case a simple analysis using cylinders were used to approximate the surface area in a single repeat unit of the BCC lattice structure and then extrapolated to determine the total surface area of the electrode. By applying this conversion factor the approximated surface area can then be used to standardise the results of the electro catalytic analysis. The approximate surface area for the three sizes of BCC lattice structure produced are shown in Table 2.6, which have been calculated on the basis of 120µm diameter beams forming the lattice structure.

<table>
<thead>
<tr>
<th>BCC Size (mm)</th>
<th>Dimension BCC Units</th>
<th>Approximate Surface Area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>3x10x12</td>
<td>1750.26</td>
</tr>
<tr>
<td>1.2</td>
<td>2.5x8x10</td>
<td>1181.32</td>
</tr>
<tr>
<td>1.4</td>
<td>2x7x8.5</td>
<td>827.21</td>
</tr>
</tbody>
</table>
3. Composite Powder Formation, Analysis, and In-Process Handling

Chapter 1 highlighted the current significant interest in additive manufacturing of composite materials, their potential to provide new and enhanced material properties in a range of application areas, but also their promise and increasing use within electrochemical applications.

This chapter will look at the process applied to combine Ti6Al4V and Expanded Graphite (EG) to form a composite powder. This powder will then be analysed in accordance with techniques overviewed in Chapter 2, to understand the changes induced through the powder preparation method including: morphology, composition and carbon structure. To maintain a more consistent analysis of powders, samples from the post printing process will be discussed simultaneously as the original fabricated composite powder, facilitating an enhanced comparative process. The post printing sample was taken after all the printed samples were produced, however due to changes in print configuration and powder handling it is unclear as to how many times the powder was cycled and subsequently printed with, the prints were done consecutively and batched out in as large a group as feasible to minimise the cycle effects. Furthermore, physical and operational modifications to the SLM50 to best utilise the developed and characterised composite material will be outlined in preparation for printing samples to be analysed in Chapter 4.

3.1. Powder Production

The primary material selected for this research was Ti6Al4V, this is because at the University of Wollongong there is significant experience with Ti6Al4V and has been used numerous times as a means to fabricate electrodes for applications in electrochemistry.[81, 84, 92, 111] This titanium alloy powder was in a spherical form with a 20-63 µm size distribution achieved through a gas atomisation process and sourced from TLS Technik GmbH (Material Datasheet provided in Appendix 3). Expanded graphite was selected as the secondary material due to its unique electrochemical viability and was produced at the University of Wollongong. [112-115] A loading value of 3wt% of EG was determined to be a good starting point for initial investigations based on previous research performed at University of Wollongong on graphene based materials, where 3wt% or less loading had shown significant changes to the behaviour of the final materials created. [114, 116, 117] Due to limited production volumes the scope of this body of research was limited down to analysing the effects for this single loading ratio of EG.

Due to the particle size (20-63µm Ti6Al4V, 0.5-1.5mm EG) and density difference (4.43g/cm³ Ti6Al4V, [118] Sub 2.25g/cm³ EG [118]) there was significantly limited applicable methods available. Simple mixing of materials of significantly different densities and particle sizes would result in segregation. Within the SLM process, segregation of the powder material would inhibit controlled and consistent welding. Carbon does not weld, and therefore it would need to be in close proximity to melting metal particles to be incorporated into the weld. Mechanically alloying is only relevant for materials of similar hardness to be merged and fused together, as such this process would not occur between the Ti6Al4V and the EG due to the comparative softness of the EG. This results in low energy ball milling being the most appropriate option to create the composite powder, as at low energy the soft material will be forced onto the surface of the harder substance effectively coating it as described in Section 1.7.3.
The process of ball milling, as illustrated in Figure 3.1B, involves having a chamber move in a hypocycloidal motion to agitate and stir the contents of the material chamber, which contains stainless steel ball bearings which impact upon the powders. Depending on the desired outcome ball mills can be operated in multiple ways. For this material, the ball milling process was run for 8 hours on a low energy setting, which allowed for the balls to press the softer graphite material onto the harder titanium particles with minimal deformation to the titanium powder. The specific ball mill used here was a Fritsch Pulverisette 7 depicted in Figure 3.1A, which enabled batch quantities of between 20-25g to be processed at a time. The titanium powder was added in with 3%wt loading of the EG powder and left for 8 hours to combine. This modified powder, for simplicity, will be referred to as Ti6Al4V-3EG. For this study, 10 batches of 20-25g were processed separately and subsequently combined to form a homogenous master mixture of composite Ti6Al4V-3EG powder, with a total of 220g produced.

![Figure 3.1 - A) Fritsch Micro Planetary Ball Mill used for the production of the Ti6Al4V-3EG composite powder adapted from [119], B) Ball Milling Mechanism adapted from [120]](image)

3.2. Imaging of Powder

The ball milling process discussed in the previous section is used throughout industry to reliably mix and coat powders. However, the process can lead to deformation of the powder/s being processed. It is therefore important to characterise the material at each stage of the powder preparation process and during the subsequent cycle life of this powder. This will provide understanding into the potential flow characteristics of the material and determine if changes in powder morphology are occurring during repeated cycling through the SLM production process, indicating cyclic limitations of the developed composite powder. The EG is soft and malleable and this can be seen illustrated in Figure 3.2A (Top Centre). In this area the sample has been deformed and flattened in the process of pressing it onto the adhesive tape. Figure 3.2B shows the Ti6Al4V powder, which has a reasonably consistent spherical morphology and the size range of 20-63µm. A representative sample of the product composite Ti6Al4V-3EG powder, prepared through the discussed ball milling process is shown in Figure 3.3A.
Figure 3.2 – Unmodified base materials used to form composite powder A) Expanded Graphite created at University of Wollongong, B) Ti6Al4V Powder from TLS Technik GmbH

Figure 3.3 – Ti6Al4V-3EG composite powders A) as ball milled unprinted Ti6Al4V-3EG, B) post printing powder

Figure 3.3A shows the ball milled resultant from the Ti6Al4V and a 3wt% loading of EG. The morphology of both starting materials has been significantly affected due to the ball milling process. The carbon flakes from the EG have been deformed and fragmented reducing the size from the original 0.5-1.5mm down to sub 100µm flakes and subsequently most have bonded onto the particles. The Ti6Al4V particles have been deformed due to the forces exerted on them from the stainless-steel ball mill media. While some particles are still spherical most have been deformed and exhibit flattening/elongation reducing the spherical quality of the original material. It would be expected for this powder to have poorer flow characteristics than the original powders, as was observed to be the case upon printing. Visually it is hard to see the differences that are occurring in the post printing medium, as shown in Figure 3.3B. The powder still exhibits similar morphology and flake distribution as seen in Figure 3.3A, however, during the printing it was noted that there was a grey powder by product forming during the printing process in and around the build tray area.
Figure 3.4 – Ti6Al4V-3EG composite powders A) grey by product weld spatter formation during printing, B) waste powder removed during sieving

Figure 3.4A shows this by product which shows significant difference to the ball milled product in Figure 3.3A, as there is an increasing number of spherical particles being reintroduced with a smoother surface finish then the coated particles. Additionally, when the powder is sieved through a 63µm sieve and the waste particulates examined (Figure 3.4B) it can be seen that this also exhibits a number of particles exhibiting increased sphericity, along with some that have characteristics of sintered morphology (Middle Left). The reason for this change in particle morphology is attributed to the spatter formation that occurs during welding processes and these shapes have been documented to have a reasonably spherical nature to them, represented in Figure 3.5. Of the three types of spatter formation and possibly the easiest to distinguish is the Type I as this has the smoother spherical morphology which allows for easier contrast in the powder. Type II and III are also likely shown in Figure 3.3B and Figure 3.4A, however due to the rough surface of the original print media it is hard to distinguish specific examples within the powder. It is important to note the colour of these spatter particles exhibit a light grey appearance as opposed to the previously dark graphite coloured appearance. There are two possible occurrences that might be causing this. Firstly, the carbon may be burning off during the weld process, supported by the observations during printing that the increased sparks coming from the weld were much larger at approximately 50-100mm as opposed to the usual 5-10mm. The second possibility is that as the spatter is forming from a molten weld pool the carbon is being alloyed into the titanium and is in turn then restoring the titanium appearance at the surface. Realistically it is likely a combination of these two aspects that causes the colour change in the material, but this will become clearer as further elemental and composition analysis occurs.
3.3. Reflectance of Powder

Understanding the interaction between applied laser light and the powder being processed is important in determining if modification of the powder, through coating with EG, will affect process parameters. For this laser-based process, understanding the absorption and/or reflectance profiles of the material is an important consideration for determining the amount of energy required to process the materials. The raw materials and the as ball milled material were analysed in accordance with the procedure outlined in section 2.1 and the resultant data shown in Figure 3.6. The results exhibit a linear trend: the upward curve at 400nm is due to glass absorption and the noise in signal attributed to the sensitivity of the internal sensor in the range of 900nm plus is due to a changeover in the internal sensors of the machine and does not necessarily represent the behaviour of the powders. The SLM50 uses a Nd:YAG laser which is the most common type used for SLM machines, at a wavelength of 1064nm, the region that is of most relevance to this study. Due to the fluctuations of the data the average was taken over the 1044-1084nm range to determine the value of interest, as shown in Table 3.1. These results identify that the composite powder exhibits more of the reflection characteristics of the graphite than the titanium, as is expected since the graphite material is on the particle surface and exposed to the light. The difference in this reflection would alter the energy density input into the materials as the process starts as the carbon deteriorates or the weld pool form this would then change the reflection characteristics again. Emphasis needs to be placed on this data as the extra energy input into the composite material would result in hotter weld pools possibly further degrading the carbon present and would likely make the material have different nominal processing parameters than the base Ti6Al4V.
Table 3.1 – Reflection properties of base powders and composite powder averaged over 1044-1084nm

<table>
<thead>
<tr>
<th></th>
<th>Averaged Over 1044-1084nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V</td>
<td>29.9%</td>
</tr>
<tr>
<td>Ti6Al4V+3EG</td>
<td>13.5%</td>
</tr>
<tr>
<td>Graphite</td>
<td>13.3%</td>
</tr>
</tbody>
</table>

3.4. EDS of Powder

Section 3.2 identified and showed that there is compositional changes occurring as the powders are cycled and since the material is a composite it is important to consider what may be occurring to the elemental distribution which is possible through EDS. EDS has a limited volume interaction and will not provide a full volumetric composition but rather only be indicative for what is occurring towards the surface of the material. It is important to note with EDS, it is ideally performed on flat surfaces to maximise the consistency of signal and volume interaction. As the powders are ideally spherical all samples were analysed on the apex as this has the lowest gradient change providing the closest flat approximate surface. Table 3.2 summarises the EDS results from analysing 10 different particles. The base powders are as they would be expected: the graphite has 99.56% carbon with some nominal trace contaminants and the titanium follows the approximately 6% aluminium and 4% Vanadium with some trace amounts of oxygen which is to be expected as titanium oxidises readily. Looking at the Pre-Print powder in Table 3.2 an average of 31.44% carbon is being detected, a significantly higher amount than the 3wt% that is known to be present due to EDS having an interaction volume that would exceed the estimated coating thickness. In an ideal scenario with 3wt% carbon and Ø30µm titanium particles approximately a 300nm coating would be achieved. Alternatively, by using Monte Carlo interaction approximations shown in section 2.4 and using the carbon percentage in the interaction volume of 31.44%, a coating thickness of approximately 430nm would be achieved which is within an order of magnitude to ideal theoretical thickness. Both coating estimates assume carbon density of 100%, but this is unlikely to be the actual density due to the random packing onto the surface that was performed.
during the ball-milling formation of the powder. Additionally, referring to Figure 3.3.A not all carbon was bonded onto the surface of the particles. Between these factors a variety of layer thicknesses have evidently occurred shown by the minimum and maximum detection range of carbon presented in Table 3.2.

Table 3.2 – EDS Results from the base powders and composite powders showing elemental compositions

<table>
<thead>
<tr>
<th>Statistics</th>
<th>C</th>
<th>Al</th>
<th>Ti</th>
<th>V</th>
<th>O</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
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<tr>
<td>Expanded</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
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<td>0.07</td>
<td>0.61</td>
<td>0.09</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Min</td>
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<td>0.07</td>
<td>0.2</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>99.56</td>
<td></td>
<td></td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.22</td>
<td></td>
<td></td>
<td>0.13</td>
<td></td>
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<tr>
<td>Ti6Al4V</td>
<td>Max</td>
<td>2.34</td>
<td>6.48</td>
<td>90.38</td>
<td>3.73</td>
<td>9.72</td>
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<td></td>
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<td></td>
<td>SD</td>
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<tr>
<td>Pre Print</td>
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<td>5.72</td>
<td>76.84</td>
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<td>0.96</td>
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<tr>
<td></td>
<td>Average</td>
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<tr>
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<td>19.15</td>
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<tr>
<td>By Product</td>
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<td>85.4</td>
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<td>0.63</td>
<td>7.42</td>
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<td>5.58</td>
<td>0.12</td>
<td>0.15</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
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<td>4.1</td>
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<td>68.46</td>
<td>2.5</td>
<td>4.86</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>9.56</td>
<td>4.8</td>
<td>79.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>5.97</td>
<td>1.74</td>
<td>5.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

With the SEM images in Section 3.2 it was theorised that the carbon content would be affected and the rise of spatter particle formation would be resulting in a decrease in the carbon content present. This hypothesis is supported by EDS. The carbon content between the different powders varies and between the preprint and post print powders the carbon decreases from 31.44% to 24.96% respectively. This decrease is most likely due to a component of the post print powder containing spatter particles that don’t have carbon on the surface, along with some carbon burnt off due to proximity to the weld pool. Further, the by-product has an even lower carbon content of 22.52%, correlating with the increase in grey smooth spherical particles formed during the weld as a result of spatter. As this ratio of titanium to carbon is changing, it can be concluded that the composite powder will be prone to degradation and as such, for this to be a viable method, it is likely an approach of continually cutting in of fresh powder would be required to maintain a stable balance. The Nickel and
Iron content observed in the EDS measurements of the Ti6Al4V-3EG are most likely due to transfer from the stainless steel balls during the ball milling process. When the results are averaged these elements do not appear, and as such these components can be deemed inconsequential.

3.5. Raman Spectroscopy of Powder

With the EDS data showing that the carbon content is changing and with the original intent of having the carbon in a form to be chemically functionalised in future studies, it is important to be able to characterise what form the carbon is in as this will dramatically impact on the chemistry. Remembering the basic analysis of the Raman response of carbon materials shown in section 2.3, by analysing the strength and shape of the G (sp2 bonds), D (sp3 bonds) and G’ (sp2 bonds) signals an interpretation of what form of carbon present is possible. The expanded graphite used in the composite material is shown in Figure 3.3, which illustrates that the G band peak relative to the D band peak ratio is very high, indicating that this is more indicative of a graphene quality carbon. However, with consideration of the G’ peak which exhibits a shoulder it can be concluded that it still contains large stacks of carbon sheets. These results are fitting as the expanded nature of this material puts it between a graphite and a graphene quality of carbon.

![Expanded Graphite](image)

**Figure 3.7 – Raman Spectroscopy of the expanded graphite powder produced at University of Wollongong**

The combination of EG and Ti6Al4V works well together for Raman analysis as titanium is a non-Raman active material. Figure 3.8 shows the Raman results for Ti6Al4V powder which shows no Raman activity. As previously mentioned carbon has multiple peaks that are distinctive and correlate to known features, meaning that any detected peaks will be due to the introduction of carbon into the samples. When these materials are combined, and ball milled together the results (Figure 3.9) exhibit significantly different carbon trait compared to Figure 3.7. This is understandable as the ball milling process has compacted the carbon onto the surface of the particles and in turn transitioned the material from being a graphene-like to more of a graphite-like carbon. Also observed is the shoulder around 600-700cm\(^{-1}\). Titanium carbide commonly exhibits multiple peaks between the 100-700 wavelength range and it is possible this is forming during the ball milling process, while inconclusive
results have been found here there have been previous studies indicating TiC formation during ball milling. [77]

**Figure 3.8** – Raman Spectroscopy of Ti6Al4V powder sourced from TLS Technik for use with the Realizer SLM50

**Figure 3.9** – Raman Spectroscopy of as ball milled Ti6Al4V-3EG powder identifying the typical curves seen and the average across the tested sample
While Ti6Al4V powder can be recycled and reused after sieving for nearly an indefinite amount of cycles, the addition of carbon into the material is affecting the number of production cycles the powder can go through. The initial concerns for this is because of the temperatures involved in that titanium melts at over 1650K and carbon bonds can start to break down above 1000K. Figure 3.10 shows for the post printing powder there are still peaks present at approximately 1300, 1600 and 2700, which correspond to the sp2 and sp3 bonds, however with the ratio of the peak at 1300 greater than 1600 this correlates with graphitic type carbon. This is expected due to the initial source being expanded graphite, however what does appear are non-Raman active results typical of uncoated titanium. From this it is possible to infer that during the printing process there is particles being reintroduced that now lack the carbon coating, represented by the SEM results shown in Section 0. Looking at the ‘By Product’ sample formed from the weld spatter (Figure 3.11), it was observed that a higher concentration of non-Raman active results were present along with the standard graphite
results. As the powder is cycled the concentration of titanium particles not coated increases and the overall carbon content is reduced, as reflected in the EDS results (Section 3).

![Figure 3.12 – Raman Spectroscopy of Ti6Al4V-3EG waste powder removed by sieving post printing identifying the typical curves seen and the average across the tested sample](image)

During the printing process it is normal for agglomerates to occur, normally due to particles that were close to the welding region and were exposed to sufficient heat to initiate sintering. These larger particles are removed by sieving and this guarantees that the powder is in an appropriate size range for the SLM50. Looking at the waste which is removed during the sieving process it can be observed that this is predominately still carbon rich powder. No Ti6Al4V results are observed meaning the waste still has primarily carbon on the surface of the particles. Referring back to Figure 3.4B the spherical particles can be seen to have some trace amount of flakes and deposits on the surface and this is likely the source of the carbon being detected. Furthermore, Figure 3.4B also showed sintered agglomerates forming, and since these particles have not been formed from the spatter it is most likely these agglomerates are responsible for the higher carbon concentrations seen in the EDS data. The Raman results for these regions support that the particles have been exposed to significant heat shown by weaker carbon peaks, meaning the quality of the graphitic carbon is decreased, as would be expected of carbon exposed to over 1000K.

### 3.6. XRD of Powder

As was highlighted in the Raman analysis there were some samples where signals were detected that might correlate to TiC formation. XRD offers a more appropriate means of trying to detect this as not all stoichiometric ratios of TiC are Raman active. [77] A comparison of the three powders tested and the printed sample is shown in Figure 3.13. Visually from Figure 3.13 the similarity of the Ti6Al4V peaks are reflected in the pre-print and post-print powders, which is understandable as it is still the major component of the composite powders. Looking at the results for Ti6Al4V in Figure 3.14A, while no card comparison exists for Ti6Al4V, there is the titanium reference card and this correlates with the peaks detected. With regard to the pre-print and post print samples the main peak difference from the Ti6Al4V results is observed at 27°, matching the reference card for graphite, as shown in Figure 3.14B and Figure 3.14C. As highlighted in Section 3.5, once the expanded graphite has been ball milled onto the particles it is compressed down into compacted graphite again which is reflected in the XRD with how consistently the peaks match up to that of graphite. While the XRD data on the powder was
not conclusive for the presence of TiC it should be noted that like the Raman method the test region is a single tightly focused point and the difficulty in consistently identifying these regions indicates that it has a low rate of occurrence. The XRD of the printed sample shown in Figure 3.13 will be discussed in Section 4.4.

Figure 3.13 – XRD Sample Comparison of Printed Sample along with baseline Ti6Al4V powder along with pre/post print composite powder samples

Figure 3.14 – XRD Analysis comparing titanium and graphite reference cards A) Ti6Al4V Powder, B) Pre-Print Ti6Al4V-c3EG Powder, C) Post-Print Ti6Al4V-3EG Powder
3.7. SLM50 Powder Handling Modifications

Efficient production of samples with consideration for the limited composite powder availability is essential. As was stated in Section 3.1, a total quantity of powder of 220g was produced. This will inherently be a limiting factor in terms of the volume and quantity of characterisation samples that can be produced and as such, hardware modifications that reduces the minimum required amount of material to produce target samples is a necessity. The normal build volume of the Realizer SLM50 (ø70mm x height 74mm) is 285 cm$^3$. Considering a loose random packing density of 0.60 [122] of spherical Ti6Al4V powder a mass of 760 g would be required to produce components within a full build envelope. Due to the limited production rate of the composite powder, non-recoverable base material cost, and considerable associated wastage it would be impractical to operate under these conditions.

Significant modifications were designed to dramatically reduce the dead volume of powder within the system and minimise the powder required to produce practical samples. These modifications had 3 main components: 1) Installation of custom wiper offsets and powder retention units, 2) Development of a reduced build volume and 3) Design, development and integration of an automatic direct feed powder hopper. With the combination of these bespoke modifications it is now feasible to produce and test small experimental material batches, with the limiting volume being that of the powder hopper of 41 cm$^3$. All modifications were designed for easy installation with no permanent modifications to the machine so that the standard system configuration could be reset when desired. Figure 3.15 shows rendered images of the unmodified standard assembly (Figure 3.15A) for direct comparison with the developed bespoke SLM50 wiper assembly with integrated powder hopper and wiper offsets (Figure 3.15B).

![Figure 3.15 – Realizer SLM50 recoater mechanism assembly A) Standard Setup, B) Modified Setup including both Wiper Offsets and Powder Hopper modifications](image-url)
3.7.1. Wiper Offsets

Due to the design requirement to minimise the operational quantity of material required to produce maximum build height prints, with the tallest samples to be approximately 25-30mm, it is important to eliminate as many areas that contain dead volume as possible. During a standard operation there is a build-up of powder along the entire wiper mechanism and this can lead to dead volumes of material that build up between the wiper assembly and the spindle that it pivots on, indicated by the dead volume region in Figure 3.16A. By creating wiper offsets, it is possible to restrict the movement area of the powder and simultaneously centre the available powder over the reduced build volume, this is illustrated in the significantly reduced dead volume surface region shown in Figure 3.16B when the wiper offsets are installed. While multiple ways to achieve this result were identified for ease of packaging with the other upgrade options a simpler approach was taken in utilising planar surface offsets to restrict movement as depicted in Figure 3.17, allowing the powder to be contained between the two wiper offsets.

![Figure 3.16 – Dead powder volume analysis in Realizer SLM50 A) Standard configuration without offsets B) Modified configuration utilising wiper offsets](Image)
3.7.2. Reduced Build Volume

As was previously stated, the standard maximum build volume of ø 70 mm with a height of 74 mm correlates to approximately 285 cm$^3$ volume of powder required for a full height build. To reduce this volume an insert was designed consisting of 3 main components: a demountable cylinder insert, a ø 20 mm piston, and a corresponding ø 20 mm build tray, as depicted in Figure 3.18. With the recoating mechanism integral to the process, it was important to take it into the consideration and insure that no component would hinder its motion, therefore the design had to be flush to the standard recoating surface of the printer. As no direct mounting points are available the attachment mechanism devised utilised a clamp with a silicone coating to prevent damage to the z-axis cylinder wall. To create the seal between the cylinder and the piston the same sealing method as utilised in the SLM50 was replicated on this smaller scale using high temperature felt, creating an adequate seal preventing powder leaking down past the piston. The small build trays were produced from Ti6Al4V bar stock to allow for the best compatibility for welding with Ti6Al4V powder. The final reduced volume was ø 20 mm with a maximum height of 35 mm resulting in a working volume of approximately 11cm$^3$, allowing for a volume of less than 4% the original working volume. Compared to the batch size being produced per day of 4.52-5.64 cm$^3$ the required number of batches to fill the build volume is drastically reduced down to only two-three batches.
3.7.3. Direct Powder Delivery Hopper

As standard on the SLM50 system, powder is fed from the powder source (approximately 850 cm$^3$ stainless steel bottle) to the process chamber by means of a single screw auger system. There is a significant associated powder dead volume with this arrangement. To accommodate the losses due to dead volume in the auger arrangement and print chamber up to 855cm$^3$ of powder (three times the maximum build volume) could be required to complete a build process that requires the maximum build volume of this system. Inefficient use of this volume of the modified powder is not practical. To negate this ineffective use of powder, an automated direct powder feed located within the wiper mechanism with a reservoir compatible to the reduced build volume was developed.

Figure 3.18 – Realizer SLM50 Reduced Build Volume Insert A) Cross section diagram of reduced build volume B) Final as produced version of the reduced build volume

Figure 3.19 – Miniature Powder Hopper for Realizer SLM50; Cross-section views of developed Direct Powder Delivery, A) In Actuated (powder loading phase) B) In Unactuated (powder release phase)
Figure 3.19 provides a cross-sectional representation of the main component assembly of the developed direct powder delivery hopper. The powder reservoir design has been tuned to hold approximately 41 cm$^3$ of material (approximately three times build volume accommodating powder at wipers). The hopper is pneumatically actuated during the standard recoating process. As shown in Figure 3.19, the short stroke (5 mm stroke) pneumatic actuator is directly connected to a multi-element shuttle valve. With each actuation the shuttle valve is loaded with 0.17 cm$^3$ of powder. This value was chosen to provide a factor of safety over the minimum required powder per layer (ø 20 mm x 25 µm) and to account for overflow between the wiper mechanisms, i.e., dead volume material. When the spring return pneumatic actuator returns to its rest position (i.e., when pneumatic pressure is removed) material at the outlet port of the shuttle valve mechanism is deposited between the wipers and in turn applied to the top layer of the build volume. To ensure synchronisation of this feed mechanisms movement and the timing of the standard wiper mechanism, the pneumatic supply for the actuator was coupled to the pneumatic source used to actuate the front silicone wiper (indicated in Figure 3.16B). Selection of this source ensured that with each recoating sweep that a distinct controlled volume of powder would be dispensed. During trials of the system, and in accordance with the standard recoating technique used for titanium powder, the powder wipe routine would be run twice for each recoating layer allowing for a total of 0.34 cm$^3$ to be deposited per cycle. Variation of the powder volume being dispensed can be achieved by actuating the wiper system multiple times per layer through modification of the recoating routine code. Alternatively, if a larger or smaller volume of powder is required, the size of the openings in the gate system can be easily modified and produced via laser cutting of Perspex sheet material.

3.8. Chapter Summary

This chapter has clearly outlined the development of a modified Ti6Al4V-3EG powder to be used as a fabrication media compatible with the selective laser melting additive manufacturing process. The composite powder that was formed has undergone thorough analysis. Through SEM imaging (Section 0) it was observed that the ball milling process induced significant changes on the particle morphology as the expanded graphite coating was being applied to the Ti6Al4V particles surface. It was observed however that particle size and appearance of the product powder was homogenous, making it a suitable starting point for testing.

Further after production cycling has occurred it showed introduction of new morphologies that are a result of spatter formation and this lead into and link with EDS. EDS (Section 0) showed that as the powders are used that the carbon content is decreasing and is at its highest point at the pre-print powder. With Raman (Section 3.5) the analysis of the carbon type present was performed, and indicated that the ball milling and transformed the expanded graphite into a graphite coating, and further that this was detectable even after cycling effects had occurred.

In addition, it was noted that the quality of the carbon did degrade and detection of non-carbon coated samples increased correlating with the EDS data and the visual observations in the SEM images. Based on some data from Raman results XRD (Section 3.6) was performed attempting to detect formation of TiC however results were inconclusive at this stage.

Now that an understanding about the powder exists it is possible to start looking at how this material will be processed efficiently including machine modifications (Section 3.7) to produce functional samples.
4. Printed Composite Ti6Al4V-3EG Sample Production and Analysis

A detailed understanding of the developed composite powder has been presented through the previous chapter. Understanding the characteristics of structures produced using the developed powder, and what effect the addition of EG has had on the final product, requires systematic and standardised analysis methods. In this chapter the standard components used for further analysis and how the print parameters were controlled and modified will be discussed. Furthermore, once the standard samples have been established, similar analysis as performed on the powder particles will be repeated, and the analysis expanded to consider additional relevant physical properties such as density, hardness, microstructure and resistivity. Structures relevant to electrochemical studies will be presented and used within a preliminary study to examine the feasibility of electrode structures produced from the Ti6Al4V-3EG composite powder in comparison to the non-modified base Ti6Al4V material.

4.1. Standard Test Components

Several different components are required for physical and electrical analysis. Boundary conditions for the geometries of these components are defined by the maximum limits of the reduced build volume. Samples must fit within the Ø20mm x 35mm build volume. An exception will be made for the electrode structures, which was feasible due to existing bespoke infrastructure (Appendix 4) and due to the comparatively low build height (12mm) which did not exhaust the supply of composite powder. Importantly, as there was a quantity of experimental Ti6Al4V-3EG powder, producing multifunctional characterisation samples was integral in efficiently acquiring a large range of knowledge from a minimum volume of material and limited number of production cycles. The developed test components facilitate mechanical testing, electrical conductivity trials and electro activity analysis.

4.1.1. Miniature Dogbones Test Sample

The “Dogbone” is a common sample type for analysing mechanical properties, as it provides relatively large, flat, regions that will be useful for further tests including: density, hardness, EDS,
Raman, XRD and EBSD. The produced dogbones are the primary sample utilised in this body of work. The specific design of the dogbone sample is based on the ASTM standard E8/E8M 2011 “Standard Test Methods for Tension Testing of Metallic Materials”, although the geometry has been uniformly scaled down by a factor of four (1:4) to be compatible with the custom build volume. An indicative sample was previously presented in Figure 2.11, whereas Figure 4.1 shows the final dimensions of the scaled dogbone. The maximum Z dimension of 25mm is in consideration of the need to allow tolerance for any support structure required to bind the dogbone sample to the ø20mm build tray, while maintaining an elegant scaling factor.

4.1.2. Electrical Conductivity Test Sample

In an effort to minimise any experimental or measurement error, it is important that the sample used for electrical conductivity studies be long and thin. The corresponding sample design had to maximise these considerations while still fitting within the reduced build volume. Figure 4.2 depicts the final design, with a sample cross-section of 2 x 0.25mm over a length of 812mm. The marginal increased height in comparison to the dogbone sample discussed in the previous section is permissible due to requirement for less support material as a result of the minimal structure cross-section. In practice, measurements were repeated multiple times to determine an average resistivity.

4.1.3. Lattice Electrode Test Samples

Three different electrode variants were to be produced, these specific configurations of electrode structures were selected based on previously unpublished research at the University of Wollongong that had established experimental testing procedures for similar structures. Additionally since the study focus was on evaluating the feasibility of composite materials for electrodes and not for the effects of the geometry, it was decided to keep the designs simple and to retain the previous electrode designs.
To accommodate standardisation of later test protocols and consistent electrode structures, a two-stage production process was adopted. Firstly, base components incorporating a threaded section for robust electrical connection were produced in batch quantities from Ti6Al4V in the standard SLM50 build volume configuration. The base components were finished by removal of supporting structures and milling of the bottom surface so that it was parallel to and consistently offset from the top surface. In the second stage, the post processed bases were fixed within a bespoke mounting plate (the arrangement of the modified base plate to enable this is documented in Appendix 4). The mounting plate accommodated up to 10 bases, upon which BCC lattice structures were printed using Ti6Al4V-3EG. Upon completion of the build process, this arrangement allowed for simple removal of electrode structures and removed risk of damage to fine lattices during manual handling.

This platform allows for a large degree of freedom in the design of the electrodes. For this body of work, and as a proof of concept, a nominal electrode boundary was defined as 12 x 10 x 3 mm. Three electrode variations were created based on a BCC lattice structure as previously shown in Figure 1.22, with repeat units of 1.0mm, 1.2mm and 1.4mm. Where necessary, the nominal size of the lattice structure was rounded down to the nearest full or half repeat unit to fit within the outer boundary, while still facilitating a self-supporting design. Figure 4.3 shows the dimensions of the 1.0 mm BCC electrode example with the nominal boundary dimensions of the lattice being 12 x 10 x 3 mm.

Figure 4.3 – Electrode Designs for Production on Realizer SLM50 Using BCC Repeat Units
A) 1.0mm BCC Electrode Structure diagram B) CAD rendering of a 1.0mm BCC Electrode
4.2. Sample Production Setup

All test samples, except lattice structures, were pre-processed using Materialise Magics. Default support structure settings for a block support type were applied. Lattice structures were pre-processed and defined using tools within the Realizer RDesigner software package. This lattice structure module allowed for the generation of thinner more detailed lattices (using a point structure exposure routine) than those which could be prepared via the Magics suite. Following pre-processing, print parameters for all samples were assigned within RDesigner and print parameters for Ti6Al4V were selected and applied to be the default base parameters for the composite material. These base parameters form a logical starting point before modification to account for process variations induced by modification of the base Ti6Al4V powder. As discussed in Section 1.6.2, there are a number of parameters that can control energy density, and as this experiment is a proof of concept the control variables will be limited to two: laser intensity (+10W, +0W, -10W) and exposure time (+10 µs, +0 µs, -10µs). Considering these variables result in nine different energy density settings, the intent being to allow observations into whether variation in energy and heat impacts the EG, significantly altering its carbon quality, or affecting material properties of produced components. The standard Ti6Al4V settings used for the +0W, +0µs conditions are provided for reference in Appendix 5. For these experiments, intensity and exposure time variations were only applied to the hatch settings, boundary and pre-hatch settings were not modified.

The two-stage printing process employed in the production of electrode structures means that after printing they are in an immediately useable form. However, the dogbone samples, and to a lesser extent the conductivity samples, require post-processing prior to use within the defined physical and electrical conductivity tests.

For XRD analysis, the sample was lightly sanded with 1000 grit sand paper to provide a flattened surface to minimise signal scattering during examination. A maximum sample thickness of 0.9mm was found to be most suitable for this measurement. The most common sample type used is shown in Figure 4.4, and included two dogbones, one was broken in half to allow mounting such that all three planes could be viewed. Samples were mounted into a hot set carbon resin and then polished using Struers Tegramin-25 as per the routine outlined in Table 4.1. EDS and EBSD testing were subsequently performed on the samples after further sample preparation by the addition of silver paint to cover nonconductive mounting clips and application of copper tape to allow dissipation of energy during imaging.
Figure 4.4 – Prepared Ti6Al4V Dogbone Sample. Sample has been mounted in resin and polished back, lastly has had conductive copper tape wrapped around base and silver paint on the sample to allow electrical dissipation during SEM analysis.

Table 4.1 – Polishing Routine used for Titanium Alloy Samples

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type</th>
<th>Time (Minutes)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diamond grinding disc 500 grit</td>
<td>4</td>
<td>Repeat as required until all Front, Top and Right planes of dogbone are visible</td>
</tr>
<tr>
<td>2</td>
<td>2000 grit wet and dry with water</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15µm diamond paste on a Struers MD-Nap magnetic plate</td>
<td>8</td>
<td>Run in 2 stages of 4 minutes until no scratches present under microscope</td>
</tr>
<tr>
<td>4</td>
<td>OP-S Colloidal silica solution (with added H₂O₂ and NH₃)</td>
<td>12</td>
<td>Run in 3 stages of 4 minutes until no scratches present under microscope</td>
</tr>
</tbody>
</table>
SLM part fabrication is inherently prone to internal stresses during the build phase. This feature is evident for components produced from this composite material resulting in the formation of significant cracks in structures during the build process, an indicative sample is shown in Figure 4.5. The formation of cracks was not found in all samples produced and most commonly cracks were found in the lowest section of the dogbone that interfaced with the support structures, however, could occur anywhere in the structure. Notably, and specifically within the dogbone samples, it was observed that as well as crack formation, the samples were difficult to handle due to a brittle nature and on first attempt several samples were broken during handling and post processing. Reliable tensile testing of these samples was therefore not possible, the cause for the initiation of the cracks was considered and proposed within Sections 4.4, 4.5, 4.6 respectively.

![Crack Formation](image)

**Figure 4.5 – Ti6Al4V-3EG dogbone example illustrating a common crack formation within the dogbone samples**

### 4.3. Density of Printed Samples

Post processing of samples through polishing enables further analysis methods to be performed, in this case density analysis was performed first. The polished surface allowed the use of optical imaging to achieve a better visual understanding of what was occurring in the printed samples. Secondly density analysis in turn provides information about the porosity of the samples which can significantly affect the material properties. For Ti6Al4V both MicroCT data and optical density were analysed. Importantly, the MicroCT data allowed for the comparison and validation of the optical methodology and as a result it was determined that optical analysis alone would provide adequate representative data for the characterisation of the Ti6Al4V-3EG samples.

Figure 4.6 shows the raw data for the nine different parameters used, with correlation not initially apparent. However, this data does not consider the energy density used for each set of parameters. Figure 4.7 describes the sample density with respect to energy density. Examining the data in this manner provides a much more intuitive and meaningful result, with the basic trend of increasing sample density with increasing energy density. This density trend is consistent with existing research; however, it has also been shown that if sufficient energy density is input a decreasing trend is observed which evidently the study done here has not gone sufficiently high enough to capture this portion of the trend. At lower energy levels, less heat is delivered into the powder bed resulting in inconsistent welds through only partial melting of particles and resulting in substantial internal porosity. Additionally, Figure 4.7 presents density data extracted from MicroCT scan data based on a 1µm³ voxel. This additional data set allows a comparative trend for the reference titanium. The trends
observed in these data correlate well with the optical methods, with variations potentially representing that larger sample groups may be required in future for better comparisons.

Figure 4.6 – Optical density values calculated from images captured on a Leica DM6000 and post processed via ImageJ software for samples printed on Realizer SLM50

Figure 4.7 – Compiled density data analysis comparing Ti6Al4V and Ti6Al4V-3EG with a comparative MicroCT result for Ti6Al4V all samples manufactured on a Realizer SLM50 and sorted by Energy Density
As previously highlighted (Section 3.3) the reflectance property of the powder to be welded may contribute to differing input energy density in comparison to the unmodified Ti6Al4V powder. Using the measured reflectance value, it is possible to correct the energy density to correlate to absorbed energy, as presented in Figure 4.8. However, direct comparison between Figure 4.8 and Figure 4.7, indicates that higher energy density is required to receive a comparable density to standard Ti6Al4V results. What this may represent is that by the addition of carbon it is acting as a weld inhibitor.

There are two possible observed effects occurring. Firstly, the modification to the powder is a thin coating of graphite. It is the thin low reflective coating that has affected change in the reflectance measurements in comparison to the base Ti6Al4V powder. It is feasible that when exposed to laser energy that the thin coating is rapidly ablated away. The rapid ablation of the coating would therefore negate any influence that the coating would have on heat transfer within the weld pool. It is proposed that this could be the reason for agreement between results in Figure 4.7 with samples displaying a similar plateau feature in values above 55 J/mm³.

Secondly, it could be that the presence of carbon at the interface between particles inhibits the weld formation and that is why even correcting for the energy density the results are significantly lower than the comparative Ti6Al4V results. This inhibiting effect may result from the in situ formation of TiC which has a significantly higher melting point of 3065°C, [118] leading to additional energy density required to achieve a sufficient melt pool temperature. Most likely it is a combination of both effects occurring. This effect on density merits further study but is outside the scope for this body of work for further analysis.

![Energy Corrected Density Comparison](image-url)

Figure 4.8 – Energy corrected compiled density data analysis comparing Ti6Al4V and Ti6Al4V-3EG with a comparative MicroCT result for Ti6Al4V all samples manufactured on a Realizer SLM50 and sorted by Energy Density

From the density analysis it is seen that to achieve comparable results in the density of printed samples in the Ti6Al4V-3EG as compared to the Ti6Al4V material, a higher energy density is required. However
comparative densities occur above 55 J/mm$^3$, and therefore in future studies the porosity can be adjusted for thorough manipulation of the printing parameters.

4.4. XRD of Printed Ti6Al4V-3EG Sample

Density analysis has shown that the composite material displays an increased porosity trends. Elemental analysis will facilitate a closer examination of the printed composite material. In the case of this composite powder, the combined presence of titanium and carbon may lead to the formation of titanium carbide (TiC) when ball milling [77] or SLM processing. [39] As such, it is important to characterise the final composition of the printed structures. XRD as mentioned in Section 3.6, offers an analysis option for TiC detection, but it is important to note with the system used it is better suited for powder-based samples. However, the system in use can still test other samples, albeit with the potential for a reduced signal response. Since the printed sample is likely to have a weak signal and may be hard to detect, a single indicative sample was selected to provide insight into the TiC possibility.

The printed sample of Ti6Al4V-3EG tested is shown in Figure 4.9, with peaks seen corresponding to Ti and TiC, with the Ti understandably being from the Ti6Al4V powder used as the base material, as shown in Figure 3.14. The TiC formation, since both titanium and carbon are present, is to be expected due to the energy that is input into the powder. Unlike in the powder samples shown in Figure 3.14 graphite has not been detected for this sample, which may be because that all carbon in the region analysed are converted to TiC.

This result indicated that there is a significant change in the product material due to the addition of a thin graphite coating. The presence of TiC is likely responsible for the brittle nature observed (noted in Section 4.2), likely due to the hardening effects of TiC and that TiC grain formations are commonly dendritic in shape with the tips of the dendrites known to act as crack initiator sites. [125] Additional analysis tools will be employed through the following sections to further investigate the material composition. In particular, EDS and Raman will provide more detail in regards to composition and region specific trends that may exist.
XRD analysis has shown that both titanium and carbon are present in the printed composite sample in the form of TiC. The distribution of elements within the sample warrants further investigation. EDS testing has been conducted on samples printed with the lowest (37 J/mm$^3$), default (50 J/mm$^3$) and highest (65 J/mm$^3$) energy density settings to provide an overview of what is occurring within the printed structures. During the analysis of these samples no differentiation due to energy density was seen to occur, as such the following figures presented have been selected to best represent the trends and are presented irrespective of the energy density.

Figure 4.10 shows three example SEM images observed across the Ti6Al4V reference samples. Typically, these samples are reasonably featureless; the only noticeable feature that occurs is the occasional pore (consistent with the relative high density of the printed material) which is inherent to the SLM process. The pores can typically be indicated by appearing nearly black on the greyscale images. These three sample areas underwent EDS analysis to further understand the distribution of elements within the region. It is important to note that since the samples are prepared and polished
using silicon and diamond abrasives, it is common that concentrated spots of carbon and silicon will be present in EDS maps.

Figure 4.10 – Typical SEM images of Ti6Al4V morphologies from printed samples captured at 5kV

EDS of the region shown in Figure 4.10A is presented in Figure 4.11 and shows the black regions observed as being carbon rich. Since there is no carbon present in this material the source can be interpreted as being from the polishing process, supported by silicon also being present in most of the carbon deposits. Furthermore, with the EDS of Figure 4.10B shown in Figure 4.12, the only surface feature detectable is a source of oxygen from localised surface oxidisation of the sample. Apart from this feature it represents a useful example of the homogenous distribution of elements that would be expected from a pre-alloyed printed sample.

Figure 4.11 – EDS of printed Ti6Al4V sample shown in Figure 4.10A, captured at 5kV
Figure 4.12 – EDS of printed Ti6Al4V sample shown in Figure 4.10.B, captured at 5kV

The EDS of Figure 4.10C shown in Figure 4.13 follows the same trends observed in Figure 4.10A, with the dark regions being sources of both carbon and silicon. The rest of the materials present are a homogenous mixture of aluminium and titanium. This consistency allows for a generalised analysis to be determined for Ti6Al4V samples, in that any black regions are a source of carbon and silicon, with the rest of the region observed a homogenous mixture of titanium and aluminium. The carbon source may be from either the resin that the sample is mounted in or the diamond polish used to prepare the surface, and the silicon present is from the polishing process. Silicon and diamond are used together
to polish the surface and the correlation between these features is due to both materials filling the small voids in the sample during sample preparation processes.

Examples of Ti6Al4V-3EG similar to the Ti6Al4V printed samples were observed to be consistent across all energy density values. As such an extract of the typical features seen is shown in Figure 4.14. Compared to the Ti6Al4V printed samples which had homogenous regions or pores, two new types of features can be seen to appear within the Ti6Al4V-3EG samples: the presence of dark grey dots and dendritic features. Figure 4.14A is further analysed in Figure 4.15 which shows the EDS data for that region. By looking at the titanium series it is possible to observe the presence of a void, further reinforced by a matching absence of aluminium and a high concentration of carbon. At this stage EDS does not provide information about the carbon state and further insight into these carbon rich deposits will be performed through Raman analysis. It is unclear if the observed carbon is from the original expanded graphite source, carbon resin or diamond paste. Further to this feature the aluminium series shows a range of regions were aluminium is not present, with reference to Figure 4.14A, these regions correlate to the darker grey areas. These same areas have slightly higher concentrations of carbon, and with the homogenous distribution of titanium it means that these regions are primarily consist of titanium and carbon and may be the locations for where titanium carbide is forming.
Figure 4.14 – Typical SEM images of Ti6Al4V-3EG morphologies from printed samples captured at 5kV

Figure 4.15 – EDS of printed Ti6Al4V-3EG sample shown in Figure 4.14.A, captured at 5kV

The EDS of Figure 4.14B shown in Figure 4.16, has similar features occurring within the darker grey regions which consists of dotted and dendritic features. However, this example from observing the titanium series which is consistent across the entire regions shows that there are no pores present. Further to this however the aluminium series has many regions where it has been displaced. This correlates to the dotted and dendritic features seen in Figure 4.14B. This correlation also supports the premise that the dotted and dendritic areas are composed of titanium and carbon deposits.
Figure 4.14C is very similar to Figure 4.14A in the types of features observed, with the EDS result for this region shown in Figure 4.17. Starting with the titanium series it can be seen that there are regions where it is absent, which correlate to the black regions seen in the SEM image (Figure 4.14C). The same regions where titanium is absent, aluminium is also absent however there is presence of both carbon and oxygen, most likely representing pores. What should also be noted in Figure 4.14C is that around the black regions there is a high concentration of the dendritic and dotted regions which are the potential sites for titanium carbide forming. If this is the case titanium carbide dendrites have been shown to be crack initiators, [125] and the voids present are most like a result of cracking from these formations.

Figure 4.16 – EDS of printed Ti6Al4V-3EG sample shown in Figure 4.14.B, captured at 5kV
By comparing all the EDS data (Figure 4.15, Figure 4.16 and Figure 4.17) back to the greyscale SEM images shown in Figure 4.14A-C, some generalisations of the compositions can be made. The SEM greyscale can provide significant insight into the samples, as SEM works on electron backscatter collection and the light and dark regions are affected by the density of the material. In regions where carbon has higher concentrations the density is less and so the image is darker, however where it is a mixture of all elements the density is higher, and the image is brighter. This combined with the elemental data can be used to surmise the composition and broken down into three typical colours: light grey, dark grey and black. Typical colour examples for Ti6Al4V-3EG samples are shown in Figure 4.18. By using this colour scale it is possible to visually observe regions via SEM imaging that will be more likely to be titanium carbide formations without performing EDS.

Figure 4.17 – EDS of printed Ti6Al4V-3EG sample shown in Figure 4.14.C, captured at 5kV

Figure 4.18 – SEM Elemental Composition Colour Spectrum based on EDS data analysed in comparison with SEM images when captured at 5kV
The SEM and EDS results for Ti6Al4V-3EG can be summarised into four common features, depicted in Figure 4.19 and include: featureless (Figure 4.19A), dotted (Figure 4.19B), dendritic (Figure 4.19C) and pores (Figure 4.19D). Pores are identifiable as previously mentioned in the Ti6Al4V analysis, with the observations of absence of titanium, and presence of carbon, silicon or oxygen coupled with a black appearance. However, with these samples, featureless regions are typical of homogenous mixture regions, shown by presence of all elements detected in those regions and a corresponding light grey colour. The dotted and dendritic regions however shown in EDS data Figure 4.15, Figure 4.16 and Figure 4.17 correspond to the dark grey regions shown in Figure 4.14A-C and represent regions where carbon has displaced aluminium, leaving titanium and carbon elements present supporting the possibility of titanium carbide formation in these regions. The regularity of these regions helps to indicate that a large portion of the carbon within the structure has potentially formed titanium carbide. As the regions observed here are on the interior part of the samples, they would have been exposed to higher melt temperatures than the external surfaces and would mean that the titanium was more readily able to react with the carbon present.

![Figure 4.19 – Ti6Al4V-3EG printed sample feature characteristics A) Featureless B) Dotted C) Dendritic D) Pores, Images captured at 5kV](image)

From what has been presented and discussed a useful example image that correlates these features is shown in Figure 4.20. This set of images highlights a range of the features previously introduced including featureless, dotted and dendritic. Dotted can be observed primarily in the bottom left hand corner (highlighted in blue shading), and by the greyscale composition it can be inferred that this region will have small localised regions of Ti and C, dispersed within a homogenous mixture of Ti6Al4V-3EG. The dendritic features which can be seen in the centre of the image (highlighted in red) have a darker colouring than the dotted areas and represent a higher concentration of the Ti and C leading to a larger displacement of Al. This displacement of Al leads to the pale homogenous areas that end up bounding around the dendritic and dotted features essentially creating a border. The region shown in Figure 4.20 illustrates no areas of voids so for an enhanced EDS image the aluminium and carbon data have been overlayed together in Figure 4.21. From the carbon distribution within the aluminium it can be seen to strongly correlate with the dark grey regions shown in Figure 4.20, with the highest concentrations shown in the dendritic structures. However, this apparent concentration change is more likely a reflection of the larger surface region for analysis as compared to the dotted regions which are much smaller and on the limit of the detector for extracting meaningful data.
Figure 4.20 – Exemplar high-resolution Ti6Al4V-3EG 3) +10W·10us SEM Image, blue region indicating dotted feature type and red indicating dendritic formation, image captured on an FEI Helios-G3 CX at 5kV.

Figure 4.21 – Exemplar high-resolution EDS Ti6Al4V-3EG 3) +10W·10us, captured on an FEI Helios-G3 CX at 5kV.
4.6. **EBSD of Printed Samples**

Discussed EDS data has definitively shown that carbon has survived the welding process and is still part of the samples, while also highlighting the most likely areas that TiC formed in. EBSD can be further used to analyse the crystal structure of the material present and determine the phase of titanium or titanium carbide type present. EBSD was performed on both Ti6Al4V and Ti6Al4V-3EG sample 5) +0W +0µs, only this sample was analysed due to the consistency seen in the EDS across the different energy densities and was selected as it represents the default titanium settings.

The Ti6Al4V sample considered is shown in Figure 4.22 and looking at the crystal orientation in Figure 4.23 distinct regions can be observed helping to depict the elongated fine grain structures. These elongated grains are typical of SLM structures for titanium due to the remelting of previous layers so the grains grow in the build direction, as found in literature and also represented in Figure 1.33. The small size of the grains is related to the rapid cooling that occurs in the SLM process as the build tray is only heated to 200°C and with the welding occurring at temperatures in excess of 1600°C this represents a significant temperature differential and the images are consistent with an 8000°C/min cooling rate. [126] The phase diagram shown in Figure 4.24 shows that the majority of this structure has an alpha phase Titanium present, meaning that it is the Hexagonal Close Packed (HCP) structure.

![Figure 4.22 – SEM Image of Ti6Al4V region considered for EBSD captured at 15kV](image-url)
Figure 4.23 – EBSD crystal orientation for Ti6Al4V captured at 15kV

Figure 4.24 – Phase colour diagram for Ti6Al4V captured at 15kV
The results for the Ti6Al4V-3EG samples were seen to be significantly different to Ti6Al4V as shown in Figure 4.25. Where Figure 4.23 is primarily composed of fine lamellar crystal grain formations this cannot be seen within the Ti6Al4V-3EG results shown in Figure 4.26. It is however shown that the dotted and dendritic features are present and these formations would appear to have disrupted the ability for the material to form lamellar grains. When TiC is introduced within a titanium matrix it has been shown to form both spherical and dendritic formations, with the tips of the dendrite formations known to be crack initiators and promote cleavage fracture behaviour. [125] These features are shown clearly in Figure 4.26. Looking at the colour groupings in Figure 4.26 it can be seen that the grain structure is significantly smaller, and that the largest grains appear to be based around the dendritic structures. Some of the grains observed were seen to be on the nanometer scale, and so between the combination of this reduced grain size and dendritic structures it would be expected that the material be prone to fractures, a finding that aligns with the observed crack formations and brittle characteristics of the printed samples. While the presence of TiC has been proven by XRD, the results shown in Figure 4.27 identify that the TiC formation is only a small percentage of the total material present in comparison to the percentage of Ti2C formation. The higher presence of Ti2C compared to TiC is due to high cooling rates and insufficient time for carbon to diffuse into the material. [39] This slow rate of diffusion is most likely the reason why pockets of the original carbon material can be observed within the printed samples.

Figure 4.25 – SEM Image of Ti6Al4V-3EG region considered for EBSD captured at 15kV
Figure 4.26 – EBSD crystal orientation for Ti6Al4V-3EG captured at 15kV

Figure 4.27 – Phase colour diagram for Ti6Al4V-3EG captured at 15kV
The overall percentage of sample phases for both Ti6Al4V and Ti6Al4V-3EG samples are summarised in Table 4.2. For Ti6Al4V the phases selected for detection were Ti-Hex and Titanium cubic as this is the alpha and beta phase of the titanium, whereas for Ti6Al4V-3EG along with the titanium phases selected, TiC and Ti$_2$C was also selected for detection. Zero solutions shown in these tables occur when the EBSD is unable to correctly index to any of the compared phases, a common occurrence due to poor sample preparation, or potentially present but not considered phases.

The zero solutions increase from 20.93% for the Ti6Al4V sample to 60.56% for the Ti6Al4V-3EG sample respectively. It is important to note that these samples were prepared in the exact same manner under the same conditions. The difference in zero solutions values is likely due to; increased hardness in the Ti6Al4V-3EG sample in comparison to the Ti6Al4V sample leading to increased polishing difficulties; the increased porosity observed through microscopy provides a non-uniform surface finish that would affect readings; and although not specifically characterised for during EBSD analysis there may be other TiC$_x$ phases present. It is recommended that for future studies it would be required to adjust the polishing procedures to better accommodate the Ti and C compounds, with electro-polishing likely to be required to minimise zero solution results.

<table>
<thead>
<tr>
<th>Table 4.2 – EBSD phase summary for Ti6Al4V and Ti6Al4V-3EG samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase Name</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Ti6Al4V</td>
</tr>
<tr>
<td>Ti-Hex</td>
</tr>
<tr>
<td>Titanium cubic</td>
</tr>
<tr>
<td>Zero Solutions</td>
</tr>
<tr>
<td>Ti6Al4V-3EG</td>
</tr>
<tr>
<td>Ti-Hex</td>
</tr>
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<td>Titanium cubic</td>
</tr>
<tr>
<td>C Ti</td>
</tr>
<tr>
<td>C Ti2</td>
</tr>
<tr>
<td>Zero Solutions</td>
</tr>
</tbody>
</table>

4.7. Raman Spectroscopy of Printed Samples

EDS and EBDS have both shown the presence of carbon, with EDS showing the possibility of regions of small carbon rich deposits still present within the printed structure, however these techniques are unable to give additional insight into what form the available carbon was in. Raman mapping and point analysis was used to analyse all printed samples. Upon analysis it was observed that all samples showed the same basic characteristics as seen in Figure 4.28 which analysed Sample 1) -10W -10µs. The lighter grey regions display no Raman active signals and was typical of titanium, however, the black regions indicated strong intensity results at the D (1350 cm$^{-1}$) and G (1570 cm$^{-1}$) bands typical of the expanded graphite that was introduced, indicating that graphitic like carbon was accessible in the printed sample. By comparing the D/G band ratio of the carbon seen in the EG 0.20 (Figure 3.7) to that of the Ball Milled Material 1.26-1.41 (Figure 3.9) a significant difference is observed. This transition is due to the compaction of the carbon layers increasing the disorder and hence the D band signal strength is increased. However, comparing the Ball milled material D/G ratio of 1.26-1.41 to that of
the carbon shown in Figure 4.28 from sample 1) it has a range of 1.20-1.30, meaning that the carbon present is comparable to the ball milled powder discussed in Section 3.5. The carbon is most likely still present due to low diffusion rates into the titanium due to the speed of manufacture and cooling rates undergone by the metals as discussed in Section 4.6.

By looking at the printed samples and considering the highest, nominal and lowest energy density printing parameters an overview of results is achieved and is shown in Figure 4.29. The results for Figure 4.29A and Figure 4.29B are very similar and comparable to the previous results shown for Ti6Al4V powder. What might appear more notable is Figure 4.29C. This is a result of a hole in the sample trapping some of the polishing compound used for preparing the samples, and is likely due to a form of amorphous carbon. The analysed area from Figure 4.29C is shown in Figure 4.30, with the source of the amorphous carbon detection from within the black region. After accounting for this variation all other Ti6Al4V results were seen to be comparable and have no variation in respect to Raman spectroscopy for all observed energy densities.
Figure 4.29 – Raman point testing Ti6Al4V printed samples
A) Sample 1)+10W +10µs B) Sample 5)+0W +0µs C) Sample 9)-10W -10µs

Figure 4.30 – Raman region analysed in Figure 4.29c for Ti6Al4V printed samples

Analysis of the Ti6Al4V-3EG results, represented in Figure 4.31, shows that there is D and G band carbon peaks present across all energy variations. Equally present are also results with no peaks representing regions of Ti6Al4V, but considering the EDS results these regions still contain carbon but
at much lower concentrations. By reviewing the D/G ratios the following results were observed: at the lowest energy density the D/G ratio was 1.64-1.87 (37 J/mm³, Sample 9), the median energy density was 1.13-1.33 (50 J/mm³, Sample 5) and the highest energy density measured 1.09-1.33 (65 J/mm³, Sample 1). With these D/G band ratios all greater than 1.00 it indicates that the carbon has a more disordered nature to it, potentially meaning that the carbon present is more available for potential reactions. There is an increasing amount of variation in carbon detected when compared to the original ball milled material, which can be expected as the graphitic carbon present has been exposed to high temperatures which has resulted in a breakdown and changes in the carbon bonds.

In summation of the observed results, all samples reveal that graphitic carbon has been seen to survive the printing process, however due to the printing conditions much of the carbon has been heat affected breaking down some of the bonds while simultaneously forming TiCₓ compounds shown by XRD and EBDS. Additionally, what was seen was Raman spectroscopy of TiC shown in Figure 4.32 and as previously mentioned in the powders TiC is most likely responsible for the shoulders observed over the 200-600cm⁻¹ with the three peaks at 260cm⁻¹, 420cm⁻¹ and 605cm⁻¹ clearly identifiable in this sample. [77] These results are significant in that it indicates that even after heat exposure in excess of 1600K it is still possible for the same material introduced in the powder stage to still be present in the printed sample. This means it may be possible to better tailor the type of carbon present to suit specific reactions or for potential functionalisation.
Previous samples have been shown on a polished sample, while this allows for a stronger signal and the ability to map regions for their composition, it is on an internal region which inherently has slightly different composition to the external regions. For the outer surface of the printed sample this region is exposed to slightly lower temperatures and powder can commonly be either sintered onto the surface or partially welded. Practically this means that this part of the printed sample will inherently more closely reflect the material properties and composition of the original composite powder. The results across all energy densities were found to be reasonably consistent, so the unmodified energy density was selected to display the results shown in Figure 4.33. The carbon on the surface of these samples can be found in three different states: Weak (Green), Graphitic (Blue) and approaching amorphous (Red). The weak results represent regions where either the carbon is being burnt off or diffused into the weld, which have more of a titanium grey appearance. The approaching amorphous results still strongly indicate the carbon signals however the clarity of the peaks are less distinguished with the G’ peak no longer appearing meaning that the carbon is significantly changing form. This indicates that these regions have likely been exposed to significant heat to affect the bonds but not enough to start to diffuse the carbon into the structure or to burn it off. The largest and most common result is for the graphitic type carbon, show by a definitive G’ peak and indicates that the carbon has a more pristine nature and correlates to the carbon seen in the composite powder in Section 3.5. Practically this means that the desired material functionality that was introduced into the powder may still be accessible at a surface level.
4.8. Vickers Hardness

Hardness is a fundamental material property and for some metals has been proven to be proportional to the tensile strength. Due to the brittleness of Ti6Al4V-3EG samples, it has not been possible to verify if the tensile data in this case exhibits a proportionality. It has however been possible to determine the Vickers hardness of the samples. In Figure 4.34 the hardness results are shown with Ti6Al4V exhibiting an average value of 392HV, a hardness comparable to wrought materials which have a documented range of 311-396HV [118], and Ti6Al4V-3EG has an average value of 547HV (averaged from 9 points). No obvious trends seem to exist in this data set, even when corrected for the energy data shown in Figure 4.35. From these results it can be interpreted that for printed samples the hardness is more of an inherent material property not dependent on the processing parameters and that by the addition of expanded graphite into the titanium it has resulted in a significant hardness increase.

Figure 4.33 – Raman Spectroscopy of External Surface for a Ti6Al4V-3EG printed dogbone, Sample 5) +0W +0µs

Figure 4.34 – Vickers Hardness testing results from Ti6Al4v and Ti6Al4V-3EG printed samples
Figure 4.35 – Vickers Hardness testing results from Ti6Al4v and Ti6Al4V-3EG printed samples arranged by energy density

The significant increase in the HV value can be potentially attributed to the formation of TiC which has a documented HV value of 3200 [122] and has raised the overall hardness of the metal. If material properties between Ti6Al4v and TiC were linear the increase in hardness to 547HV would correspond to approximately 5.25% TiC. The EBSD data for the small region analysed showed TiC to be 5.01% meaning that this trend is plausible, with the difference likely being due to compositional changes over the entire sample or other more complex material properties and microstructure considerations. However if we consider the Ti2–C content of 27.29% and a 2447HV [123], the resultant printed material should have had a hardness of 1093HV. This value is even further away from the measured material hardness, it is possible however then that the Ti2–C value may not be an accurate representation for the distribution throughout the printed sample. Additionally the source that published the Ti2–C value of 2447HV also stated that different phases of titanium present in the material are likely to be contributing to fluctuations in the hardness for nonstoichiometric ratios of TiC. [123] This effect may be one of many influencing factors resulting in the lower measured value of 547HV.

The measured value of 547HV for a Ti6Al4V-3EG composite is comparable to another study where a Ti/TiC matrix was formed with a 12.5% TiC content via SLM and a Vickers hardness of 577HV achieved. [58] By using the hardness value for the final material and the Titanium used, if the trend was linear then the approximate TiC formation would correlate to 15-16%, however during the process the addition of TiC was controlled at a concentration of 12.5%. This difference could easily be a result of changes in the processing conditions, SLM hardware, variations in base material hardness or formation of unconsidered TiCx components. With these studies a proportionality in TiC content to Vickers hardness is exhibited, further research would be required to better quantify this relationship.

4.9. Electrical Resistivity of Printed Samples

The preceding sections have documented the physical material properties of the developed composite Ti6Al4V-3EG powder once processed under a varied set of SLM operating parameters. A further consideration that is essential to this body of work is the electrical properties of the produced material.
and how these properties may benefit future studies in the area of electrochemistry. This preliminary electrical conductivity investigation will look at the resistivity of one sample as outlined in Section 4.1.2. This sample will provide insight into the effects on resistivity that have resulted from the addition of the thin graphite coating to the base powder and the compositional changes that have been induced during the SLM process.

Using the method described in Section 2.8, resistivity was determined, and values are summarised in Table 4.3 along with documented and theoretical values as comparisons. The measured electrical resistivity value of printed Ti6Al4V differs, exhibiting a 29% variance with respect to the documented bulk value for this alloy. This error is attributed to the different fabrication and measurement techniques involved, although at present no appropriate comparisons could be found in literature. Using this measured resistance value in combination with a documented carbon resistance value a theoretical resistance value of 4.23E-4Ωcm can be determined for the composite material if linear trends are assumed. However as previously mentioned 5.01% TiC has been formed, the documented resistivity value for TiC of 2.15E-4 would actually imply that the resulting printed component should have had a lower final resistivity. What is likely occurring is that internally the TiC is lowering the resistivity but externally the carbon still present in an unreacted state as shown by the Raman is likely increasing the resistivity. If this effect is being interpreted correctly then linear interpolation is a poor means of attempting to calculate the resistivity for the part and a more accurate means would have to be researched for further analysis. Whatever effect that is occurring the practical result shows merit in being able to modify the resistivity through variance of the initial graphite coating thickness, however further research is required to adequately model the printed materials resistance distribution.

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<tr>
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<tr>
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</tr>
<tr>
<td>Ti6Al4V+3EG (Printed)</td>
<td>5.21E-4</td>
</tr>
</tbody>
</table>

4.10. Electrochemistry of Novel Lattice Structures

With the in-depth knowledge of the print media and printed samples being established and it can be concluded that EG survives the print process and is clearly present at the surface of the printed structures. In order to probe the nature of the material accessible at the surface a simple electrochemical study was performed by carrying out a cyclic voltammogram on 1.2BCC and 1.4BCC structures both with and without EG as shown in Figure 4.36 and Figure 4.37 respectively.
Initial observations for the results achieved in Figure 4.36 and Figure 4.37 demonstrate a capacitance effect indicated by the broadening of the graph at 0V, a charging effect typical of graphitic materials, [127] and because of the electron interaction that occurs on the edge of the carbon layers which is
where additional functional groups can be bonded to enhance the reaction. [128] Effects of such functional groups can be observed in the reversible redox couple seen at -0.1V which is representative of surface defects such as carboxyl/carbonyl structures. Electrode enhancement is more significantly evident in the Oxygen Evolution Reaction (OER) that occurs while a positive potential is being applied, with the peak current improved by approximately a factor of six for both the 1.2BCC and 1.4BCC electrodes. This enhancement to the OER which is not evident in the Ti6Al4V material identifies a significant lowering of the potential required to cause oxidation of water for the formation of O₂ and only requires 0.8V for the Ti6Al4V-3EG material. There may be a similar effect occurring at the Hydrogen Evolution Reaction (HER) that is being obscured by the capacitance effect, additional studies are required further investigate these effects.

When the different sizes of Ti6Al4V-3EG electrodes are compared in Figure 4.38, once the result are standardised there is no significant difference observed. The small variation is most likely due to the surface area approximation used to standardise the results. This indicates that no significant effects are occurring due to changes in lattice geometry and that the size of the geometry is not limiting the reaction rate.

![Comparison of Ti6Al4V-3EG Electrodes](image)

*Figure 4.38 – Cyclic Voltammogram of Ti6Al4V-3EG Electrodes, 2nd Cycle at 100mVs Positive Scan with Eᵢ = 0V and Standardised by surface area*

From these results it can be concluded that there is electro active carbon available at the surface of the electrode that is enhancing the reaction, meaning that this material may have future applications where OER reactions are of interest. Carbon can be chemically modified to change how it reacts, allowing for potentially tailoring the functional groups to modify electrodes for specific reactions. Further investigations are required to evaluation this option.

### 4.11. Printed Sample Summary

Through the production and analysis of printed samples several insights have been gained into the developed novel Ti6Al4V-3EG composite material. Density (Section 4.3) measurements performed
through optical microscopy showed that the composite material has a higher level of internal porosity than Ti6Al4V reference samples. Reduced density is likely due to the formation of TiC increasing the viscosity of the melt pool and decreasing the flowability of the melt pool. EDS (Section 4.5) was subsequently used to highlight that there are pockets of high carbon composition within printed Ti6Al4V-3EG samples, however these regions are inconsistent in size and distribution, as well as regions of homogenously mixed elements.

EBSD analysis was performed to gather greater detail on the observed compositional distributions. EBSD (Section 4.6) detected the distinct presence of TiC and Ti2C in the Ti6Al4v-3EG sample, and results imply that more forms of TiC may be present. The high concentrations of carbon shown in EDS correlate with the carbide locations shown in EBSD. Further the EBSD showed a fine microstructure, which along with distributed dendritic features (known crack initiators) are the source of the brittle nature of the printed samples. The XRD performed (Section 4.4) also indicated the presence of carbides further supporting the case that they are distinctly present throughout the entire sample leading to an increased hardness over the Ti6Al4V reference sample (Section 4.8). Variance of the print parameters was not observed to affect the measured hardness value, indicating that the resultant hardness is as a result of the volume of added carbon.

EDS and EBSD have shown that carbon is dispersed throughout the sample with some areas showing higher concentrations. Raman Spectroscopy (Section 4.7) was performed to analyse the type of carbon present. The Raman indicated that while most carbon had been degraded similar to effects that were present in the powder analysis (Section 3.5) there are still distinct regions of carbon that remain unmodified with respect to the starting material and was more prevalent on the perimeters of the geometry. This carbon effect on the surface was as a result of lower temperatures and the particles being only partially welded or sintered. From this point with the presence of the graphite quality carbon at the surface, basic electrode characterisation was performed. The results of this showed an increase in reactivity of the electrodes especially at the OER and confirmed that electroactive carbon is the reason for this enhancement. These results help support the merit for future investigations into potential uses and applications for composite materials within electrode structures.
5. Conclusions and Future Work

5.1. Conclusion

This thesis has aimed to create a composite material comprised of up to 3wt% loading of Expanded Graphite coated onto a Ti6Al4V powder and process it within a Realizer SLM50 to produce tangible three-dimensional components. There were three main objectives targeted to evaluate the success of this body of work.

1) Development of methodology to produce a composite material comprising of Ti6Al4V powder from TLS Technik GmbH and 3wt% EG, while maintaining a powdered feedstock appropriate for use with SLM.
2) Improve the capabilities of the SLM50 to work with small research volumes of experimental material so as to conserve the limited amounts of print media.
3) To produce 3D printed samples suitable for structural, mechanical and electrochemical analysis; and to characterise these and the feedstock powder in order to understand how the addition of carbon into the print media affects the printing process.

Objective 1: A key requirement of the modified Ti6Al4V-3EG powder was compatibility with the selective laser melting additive manufacturing process. Ball milling of the EG onto the Ti6Al4V powder was noted to change the morphology of the powder, as observed through SEM imaging (Section 0). This change in morphology was not found to significantly affect the applicability of the powder to the SLM process as comparable powder flow ability was maintained. However, it was found that the ball milling had compacted the EG onto the surface of the spherical particles making the coating more representative of graphite than expanded graphite.

Objective 2: Extensive machine modifications were made to the SLM50 (Section 3.7) in order to make the commercial system capable of handling the smaller powder volumes typically available in the research and development process. These modifications were made to retrofit into the machine without requiring permanent hardware modification, or access to programming controls. Bespoke modifications were rolled out under three main components: Wiper modifications, reduced build volume, and a synchronised feed powder hopper. The wiper offsets allowed reduction of dead material volume while keeping the powder centred over a reduced build volume. When the system was run it was not efficient or effective to pause or load in powder manually as it posed a high risk to causing print failures, thus a powder hopper was created that linked into the existing pneumatic actuation for the recoater mechanism and automatically dispensed a controlled volume of powder with each recoating sequence. The combination of these three components allowed for a build volume of ø20mm diameter with 35mm height and with only 40cm³ powder required for a full volume print. These modifications facilitated the efficient implementation of new R&D quantities of materials with the SLM50.

Objective 3: Production and analysis of printed samples have offered several insights into the developed novel Ti6Al4V-3EG composite material. Density (Section 4.3) measurements performed through optical microscopy showed that the composite material has a higher level of internal porosity than Ti6Al4V reference samples when printed. Reduced density is likely due to the formation of TiC increasing the viscosity of the melt pool and decreasing the flowability of the melt pool. The existence
of internal pockets of carbon within welded structures was shown through EDS analysis (Section 4.5), however these regions of high carbon concentration are inconsistent in size and distribution. EDS also showed that some of the carbon regions contained titanium but had displaced aluminium and vanadium, additionally there was also completely homogenous regions detected.

EBSD analysis was performed to gather greater detail on the observed compositional distributions. EBSD (Section 4.6) detected a distinct presence of TiC and Ti$_2$C in the Ti6Al4V-3EG sample, and results imply that more forms of TiC may be present. The high concentrations of carbon shown in EDS correlate with the carbide locations shown in EBSD. Furthermore, EBSD showed a fine microstructure which along with distributed dendritic features (known crack initiators) are the source of the brittle nature of the printed samples. The XRD performed (Section 4.4) also indicated the presence of carbides, further supporting the case that they are distinctly present throughout the entire sample leading to an increased hardness over the Ti6Al4V reference sample (Section 4.8). Variance of the print parameters was not observed to affect the measured hardness value, indicating that the resultant hardness is as a result of the volume of added carbon.

EDS and EBSD have shown that carbon is dispersed throughout the sample with some areas showing higher concentrations, Raman Spectroscopy (Section 4.7) was performed to analyse the type of carbon present. The Raman analysis indicated that most carbon had been degraded and displayed similar to effects to that present in the powder analysis (Section 3.5). However, there are distinct regions of carbon that are of comparable quality to what was initially introduced and is more prevalent on the perimeters of the geometry. This carbon effect on the surface is as a result of lower temperatures and the particles being only partially welded or sintered.

Post print analysis of the print media (i.e., after production cycling) by SEM confirmed the presence of a range of new particle morphologies that were a result of weld spatter formation. EDS confirmed that as the powders are used that the surface carbon content is decreasing and is at its highest point at the pre-print powder (Section 0). Raman analysis of the carbon types was performed and indicated that similar carbon as detected in the pre-printing powder was found (Section 3.5). Along with graphitic carbon on the powder, it was observed that with cycling of the print media a reduction in the quality of the carbon did degrade and detection of non-carbon coated samples increased correlating with the EDS data and the visual observations in the SEM images. Based on some data from Raman results, XRD (Section 3.6) was performed in an attempt to detect the formation of TiC. However, results of this further analysis on the print media were inconclusive.

Given that the resultant structures had a significant amount of graphitic carbon present, a series of basic electrochemical investigations were undertaken to determine the ability of the printed structure to behave in a REDOX device. It was noted that the carbon associated with these printed structures were electrochemically accessible and increased the surface capacitance of the electrodes while providing an enhancement of the oxygen evolution reaction (OER) via a reduction of the onset potential with respect to an unmodified Ti6Al4V structure. The development of the capacitance effect was typical of an electrochemically active carbon such as multi-layered graphene.

5.2. Future Work

Based on this work there are still a significant number of future avenues for research to be able to further refine composite materials for use with SLM and these include:
• Composite powder scale-up: While the SLM50 is now modified for use with small volumes of powder, looking into avenues that can achieve higher production rates than 4.5cc per day will increase the size of potential structures that could be produced for research as not everything can be miniaturised.

• Improvement of composite powder fabrication methods: This requires research into alternatives to ball milling that may not be as destructive to the quality of the carbon being added in and includes concepts like CVD or rotary evaporation.

• Systematic variance of the loading level of expanded graphite within the composite material and how that relates to changes of the material or electrochemical properties.

• Alternative composite materials such as steel or aluminium: While Carbon and Titanium alloys have been shown to produce an interesting material there may be other combinations that might alloy for a more mechanically stable material while maintaining an enhanced electrochemical capability.

• Functionalising the carbon on the electrodes surface: This may prove an effective way to increase reactivity of an electrode or enable more specific application areas such as water splitting.

• Comparative studies of composite structures such as coatings: This work has focused on incorporating the secondary material into the structure but this may not be the best means to introduce a secondary material.
References


103. JEOL, High Power Optics JSM-7001F/JSM-7001FA.


Appendices

Appendix 1

Image J Script for optical Density Analysis

```java
current = "Titanium Graphite/";
sample = "5) +0W +0us/";
plane = "Front_Plane/";

indir = getDirectory("current") + current + sample + plane;
outDir = indir + "IJP_" + plane;

list = getFileList(indir);

File.makeDirectory(outDir);

for (i=0;i<list.length;i++){

    open(indir + list[i]);

    //Create Copy
    run("Select All");
    run("Copy");
    w = getWidth();
    h = getHeight();
    original = getTitle();
    temp = getTitle() + ".Threshold";
    newImage(temp, "8-bit", w, h, 1);
    run("Paste");

    selectImage(original);
    close();

    selectImage(temp);
    run("Colors...", "foreground=white background=black selection=yellow");
    run("Options...", "iterations=1 black count=1");
    run("8-bit");
    run("Set Scale...", "distance=1 known=1 pixel=1 unit=1 global");

    //thresholding
    //run("Auto Threshold", "method=Intermodes");
    run("Auto Threshold", "method=Triangle");

    //Cleanup
    run("Median...", "radius=11");
    run("Remove Outliers...", "radius=60 threshold=10 which=Dark");
    run("Remove Outliers...", "radius=9 threshold=50 which=Bright");
```

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run("Despeckle");

// Analyze
run("Analyze Particles...", "size=0.00-40000 show=Overlay include summarize");

selectImage(temp);
saveAs("tiff", outDir + temp);
close();
}

// Save Data
selectWindow("Summary");
saveAs("Text", indir + "ParticleSummary.txt");

// Black & White Counts
run("Clear Results");
list2 = getFileList(outDir);

nBins = 256;
row = 0;

for (i=0;i<list2.length;i++){
open(outDir+list2[i]);
BWImage = getTitle();

getHistogram(values, counts, nBins);
setResult("Name", row, list2[i]);
setResult("Black", row, values[0]);
setResult("B_Count", row, counts[0]);
setResult("White", row, values[255]);
setResult("W_Count", row, counts[255]);
row++;

updateResults();
selectImage(BWImage);
close();
}

saveAs("Results", indir + "ColourCount.txt");
Appendix 2

Matlab Micro CT image post processing code

```matlab
function Image_Processing_Whole_Picture
(Startslice,numslice,workingfolder,patternname,fileformat,OriginalImageLength,OriginalImageWidth,outputpattern,outputfolder,Pixel_Width,Filter_lvl)

tic;
Imagearray = single(Batch_Image_Read_PS
(Startslice,numslice,workingfolder,patternname,fileformat,OriginalImageLength,OriginalImageWidth));
timeread = toc;

[Picture_Width,Picture_Length,Picture_Depth] = size(Imagearray);

TempArrayLength = Pixel_Width + 2*Filter_lvl;
No_Segments = ceil(Picture_Length/Pixel_Width);
Temparray = single(zeros(size(Imagearray)));

tic;
for i = 1:No_Segments

if i==1
    StartPixel = 1;
    EndPixel = Pixel_Width + Filter_lvl;
    Tempstartpixel = Pixel_Width*(i-1)+1;
    Tempendpixel = Pixel_Width*(i);
elseif i<No_Segments
    StartPixel = Pixel_Width*(i-1) - Filter_lvl +1;
    EndPixel = Pixel_Width*(i) + Filter_lvl;
    Tempstartpixel = Pixel_Width*(i-1)+1;
    Tempendpixel = Pixel_Width*(i);
else
    StartPixel = Pixel_Width*(i-1) - Filter_lvl +1;
    EndPixel = Picture_Length;
    Tempstartpixel = Pixel_Width*(i-1)+1;
    Tempendpixel = Picture_Length;
end

Processingarray = Imagearray(:,StartPixel:1:EndPixel,:);
Holdingarray = zeros(size(Processingarray));
Holdingarray = medfilt3(Processingarray,[Filter_lvl Filter_lvl Filter_lvl],'replicate',1);
%Holdingarray = Processingarray;

if i>1
    Holdingarray(:,1:Filter_lvl,:) = [];
end
if i<No_Segments
    Holdingarray(:,(Pixel_Width+1):end,:) = [];
end
Temparray(:,Tempstartpixel:Tempendpixel,:) = Holdingarray;
%Temparray = cat(2, Temparray, Holdingarray);
clearvars Holdingarray Processingarray;
```
end
timeprocess = toc;

Imagearray = logical(Temparray);
tic;
Batch_Image_Write_PS
(Startslice,numslice,outputfolder,outputpattern,fileformat,Imagearray);
timewrite = toc;

totaltime = (timewrite + timeprocess + timeread)/60;
disp(['Total Time taken to Process Images (min) ' num2str(totaltime)]);
end

function Batch_Image_Write_PS
(Startslice,numslice,outputfolder,outputpattern,fileformat,Imagearray)

Endslice = Startslice + numslice - 1;

% [M,N,Q] = size(Imagearray);

for k = Startslice:Endslice
    i = k+1-Startslice;
    % Create an image filename, and read it in to a variable called imageData.
    tiffFileName = strcat(outputpattern, num2str(k), fileformat);
    FullFileName = fullfile(outputfolder, tiffFileName);
    TempImage = Imagearray(:,:,i);
    imwrite(squeeze(TempImage),FullFileName);
end

disp('Image Write Complete');
end
Appendix 3

TLS Technik Powder Size and MSDS

<table>
<thead>
<tr>
<th>Ti6Al4V Powder Sieved Size 20-63µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{10}$</td>
</tr>
<tr>
<td>$D_{50}$</td>
</tr>
<tr>
<td>$D_{90}$</td>
</tr>
</tbody>
</table>
Appendix 4

Drawings for custom tray for using pre-printed electrode bases
## Appendix 5

### SLM50 Ti6Al4V Hatching Settings

#### Ti6Al4V Parameter Settings for 25µm Slices on SLM50

<table>
<thead>
<tr>
<th>Process Conditions</th>
<th>Build Tray Temp: 200°C</th>
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<tbody>
<tr>
<td></td>
<td>Oxygen Target: 0.2%</td>
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<table>
<thead>
<tr>
<th>Scan Definition</th>
<th>Boundary</th>
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</thead>
<tbody>
<tr>
<td>Exposure</td>
<td>60µs</td>
</tr>
<tr>
<td>Point Distance</td>
<td>30µm</td>
</tr>
<tr>
<td>Laser Power</td>
<td>42.5W</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pre – Hatch</th>
<th>Exposure: 60µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point Distance</td>
<td>30µm</td>
</tr>
<tr>
<td>Laser Power</td>
<td>42.5W</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hatch</th>
<th>Exposure: 80µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point Distance</td>
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</tr>
<tr>
<td>Laser Power</td>
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<table>
<thead>
<tr>
<th>Fill Line</th>
<th>Exposure: 80µs</th>
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</thead>
<tbody>
<tr>
<td>Point Distance</td>
<td>30µm</td>
</tr>
<tr>
<td>Laser Power</td>
<td>42.5W</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hatching</th>
<th>Pre – Hatch</th>
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</thead>
<tbody>
<tr>
<td>Hatch Offset</td>
<td>0.05mm</td>
</tr>
<tr>
<td>Hatch Spacing</td>
<td>0.25mm</td>
</tr>
<tr>
<td>Rotate Hatch</td>
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<table>
<thead>
<tr>
<th>Hatch</th>
<th>Hatch Offset: 0.05mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatch Spacing</td>
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<td>Rotate Hatch</td>
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<tr>
<td>Stripe Height</td>
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