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**Feature Size Dependent
Manufacturability Influences the
Functional Properties of Ti-6Al-4V
Micro-Strut Lattices Fabricated through
Powder Bed Fusion**

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Abstract

Powder bed fusion (PBF) additive manufacturing techniques have enabled the fabrication of geometrically complex porous metallic lattice structures. Applied to biomedical implants such lattices offer many advantages over traditional non-porous implants, by allowing tissue ingrowth and more closely recapitulating the stiffness gradients of the native tissue. Despite these advantages, defects inherited from the fabrication process can act to limit structural and mechanical integrity. On account of a reduced feature size, these defects are inherited disproportionately in the micro-strut building blocks of the lattice. This is understood to drive a degradation of mechanical properties compared to traditional bulk-sized components. In this work, we show that this stems from a number of characteristics passed on from the fabrication process. This extends to a disproportionate inheritance of internal porosity, which may arise due to increased cooling rates on account of a higher surface-to-volume ratio; microstructural refinements, which similarly may arise due to increased thermal gradients; and surface defects, which in small diameter struts may account for a much larger portion of the total material volume. By studying these characteristics systematically, and as a function of different strut diameters, we were able to gain an understanding of their individual contribution towards mechanisms of deformation and failure in micro-strut lattices. Furthermore, by adopting standardized micro-strut dog-bone geometries, we were able to isolate geometrical variations between lattice designs, and characterize the bulk mechanical properties of the material, rather than the engineering mechanical properties of the lattice. Among the process inherited characteristics that were investigated, surface defects such as partially adhered powder were shown to be particularly detrimental to both the quasi-static and fatigue properties of micro-struts. These defects act as stress concentrations, which act as critical sites for crack initiation and modify the development of local plasticity; as well as account for a significant portion of the total material volume, and consequentially lead to a reduction in load-bearing capacity. As these defects are largely unavoidable, biomedical implants fabricated through PBF usually require a further surface cleaning post-processing step. However, traditional post-processing techniques such as grinding or polishing are ill-suited to lattice structures due to the lack of a line of sight to internal features. Chemical etching does not have this issue, and in this work was successfully employed for refinement of the as-built surface in lattice structures. Using the micro-strut dog-bone geometries, the resulting improvement in mechanical properties could be characterised alongside the gradual removal of surface defects. In addition to mechanical properties, the overall success of orthopaedic implants is driven by cellular responses at the implant surface. Therefore, this work was also extended to examine the influence of chemical etching on cell-substrate interactions. *In vitro* assessment revealed that chemical etching influenced

osteogenesis. As surface defects were removed, greater cell spreading was observed, suggestive of osteogenic differentiation, and accompanied by enhanced mineralization.

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Chapter 1: Introduction

1.1 Clinical strategies for bone repair

Bone is a dynamic tissue with an inherent ability for continued remodelling and self-repair. Despite this, a number of situations may arise where bone will not heal naturally over the course of a lifetime [1], [2]. This extends to defects above a critical size, or pathologic non-healing segments of bone. In such instances, clinical intervention is required for repair. Most commonly, this is achieved by transplanting a bone graft [1], [2]. However, this approach is also associated with a number of disadvantages. When autografts are used, this revolves around donor site morbidity and limitations of the volume of bone which can be harvested. Allografts and xenografts are also used. However, these approaches have their own disadvantageous, concerning challenges associated with osteointegration, and the risk of eliciting an immunogenic response [3].

Bone tissue engineering has great potential for bone repair while also circumventing many of the problems associated with traditional bone grafting [4], [5]. These strategies aim to introduce new engineered bone grafts, typically taking the form of a scaffold. Depending on the method of fabrication, engineered scaffolds may also offer an enhanced level of design freedom [6]. Consequently, bone tissue engineered scaffolds may be more suitable for complex defect morphologies, as well as potentially imparting enhanced implant functionality. These advantages have led to continuing research efforts to identify biomimetic materials and structures suitable for bone tissue engineering [7].

Among these materials, Ti-6Al-4V has emerged as a favorable option for osteo integrated bone implants. This largely stems from excellent corrosion resistance and biocompatibility. Although the alloying components of Ti-6Al-4V, specifically Vanadium, has been cited as potentially cytotoxic, titanium has a strong affinity for oxygen, resulting in the spontaneous formation of a passive surface oxide film [4]. As result, the metal from the environment, and the material exhibits excellent biocompatibility.

Titanium alloys also exhibit comparable mechanical behaviour to long bones. This extends to a high strength to weight ratio, which is required for efficient movement yet also skeletal rigidity [4], [5]. After implantation, implant stiffness may shield the surrounding tissue from mechanical stress, and lead to bone reabsorption. Although the stiffness of titanium alloys is comparable low with other biomaterials, it still exceeds that of bone, and some stress shielding can still occur [4]. Advances in manufacturing may negate these effects, enabling the fabrication of geometrically complex porous lattice structures, which can more closely recapitulate the stiffness gradients of the native tissue [8], [9].

1.2 Additively manufactured metallic lattice structures

Among advanced methods of fabrication, powder bed fusion additive manufacturing techniques are well suited to the fabrication of geometrically complex metallic lattice structures [10], [11].

1.2.1 Industry uptake

Applied to orthopaedic implants and bone tissue engineering, the level of design freedom, and small feature resolution of PBF techniques have enabled a considerable level of implant customization and functionality [4]. These many advantages over traditional techniques, such as casting or machining, have resulted in a considerable uptake of PBF manufacturing for medical devices. A growing number of additively manufactured medical devices have been FDA or EMA approved for commercialization in the past few years. This extends to the Titanium® TL curved posterior lumbar cage developed by Stryker, or the ATTUNE Cementless® knee implant with AFFIXIUM™ 3DP technology developed by Johnson & Johnson [12], [13]. By allowing bone ingrowth, these implants have enabled an enhanced level of stability and osteointegration, meeting the demands of a growing population of more active patients. Moreover, additive manufacturing has ushered in a new era of implant customization. Patient-specific implants such as the TRUMATCH® CMF cranio-maxillofacial implant developed by Johnson & Johnson, or the Osstec™ Osseo-integrated Implant developed by Osstec exemplify the potential of this technology [14]. These implants are tailored to the unique anatomy of each patient, allowing for a more precise fit and improved surgical outcomes.

1.2.2 Manufacturing limitations

Despite the advantages of PBF techniques, defects and microstructural characteristics inherited from the fabrication process can result in a degradation of mechanical and biological properties [15], [16]. This extends to the inheritance of internal porosity, a refined α' martensite microstructure, and topological defects primarily taking the form of partially adhered powder [17], [18]. Fortunately, the majority of these effects can be minimised through refinement of in-process printing parameters, and post-processing techniques. However, on account of a reduced feature-size, characteristics of the fabrication process are often inherited disproportionately in the micro-strut building blocks of the lattice, and may lead to a degradation of mechanical properties compared to traditional bulk-size components [19], [20]. Recently, this degradation of mechanical properties has been investigated using standardised micro-strut dog-bone geometries [19]. This has allowed researchers to isolate geometrical variations between different lattice designs, and study the bulk mechanical properties of the material. From this work, it is

becoming apparent that mechanical properties are sensitive to even small changes in the strut diameter. However, there are a number of process inherited factors which may drive these effects, and further work is required to understand the uptake, and individual contribution of each factor towards methods deformation and failure in micro-strut lattices.

Among the characteristics inherited from the fabrication process, topological defects such as partially adhered powder may also influence the success of the implant, by driving modified cell-substrate interactions through mechanotransduction [21]. This is also influenced by modification of the as-built surface through post process surface cleaning; which is typically required in biomedical implants, to reduce the risk of partially adhered powder becoming dislodged *in vivo*, and to improve mechanical properties [22], [23], [24]. Although it is becoming apparent that both overly rough and overly smooth surfaces can be detrimental to osteogenic differentiation, these studies are still lacking for additively manufactured metal surfaces, and there is no consensus on an ideal roughness value [21], [25].

1.2.3 Limited implant functionality

An enhanced level of implant functionality is achieved by the capability of PBF to manufacture lattice structures with a high degree of resolution. Applied to orthopaedic implants, features such as lattice architecture, pore size and strut diameter can be designed to achieve a tailored mechanical and biological response [4]. The high resolution of PBF has lent itself well to such applications, where subtle changes (in the order of a few tens of microns) in strut diameter or pore size can have a significant impact on the properties of the implant, and the likelihood of surgical success. Despite this high resolution, and as discussed in Section 1.2.3, defects can be inherited from the fabrication process [26]. This results in variations between the as-designed and as-fabricated geometries, limiting the potential to tailor the properties of the lattice for a defined response [20]. These defects impact not only the geometrical aspects of the lattice but also the material properties. For example, surface defects act as stress concentrations, and may lead to premature fatigue failure. From a design perspective, the characterisation of material properties is fundamental to the prediction of mechanical performance and failure mechanisms, and as a result, these defects significantly impeded our ability to design such implants for a specific function.

1.2 Research focus/objectives

This work investigates the manufacturability of micro-strut lattices fabricated by powder bed fusion, and applied to biomedical implants. In-process and post-process

manufacturability are assessed as a function of feature size, with the objective of optimising micro-strut material properties, and cell-substrate interactions.

The research objectives are described below.

1. Produce fully dense material in micro-strut lattice samples using SLM.
2. Examine the uptake of process inherited defects in small diameter struts, and the resulting effect on mechanical properties.
3. Implement post processing techniques for the removal of process inherited defects which were detrimental to mechanical properties.
4. Examine the potential improvements in mechanical properties, as well as the biological implications of using such post processing techniques for biomedical implants.

1.4 Thesis structure

To achieve the objectives of this research, the thesis is divided into seven chapters as described below.

- **Chapter 2, Literature Review:**

Chapter 2 provides an insight into the literature most relevant to this work. This extends to an overview of bone biology, and to an introduction to using additive manufacturing techniques for the fabrication of porous metallic biomaterials for bone repair. Following this, we discuss the suitability of selective melting for such applications. This extends to a review of common characteristics inherited from the fabrication process, as well as their implications on mechanical and biological properties.

- **Chapter 3, Feature size specific processing parameters for Ti-6Al-4V micro-strut lattices fabricated by powder bed fusion:**

Chapter 3 examines the basic manufacturability of micro-strut lattices compared to traditional bulk components with no in-designed porosity. The focus of this study is to maximise relative density, for which it is well established is a prerequisite for achieving good mechanical properties.

- **Chapter 4, Morphological and microstructural characteristics of additively manufactured Ti-6Al-4V micro-struts determine feature size dependent tensile and fatigue properties:**

Chapter 4 examines the uptake of other process inherited defects in small diameter struts. This extends to a characterisation of surface roughness, strut morphology, and microstructure, as a function of strut diameter.

Particular attention is paid to relating these factors to mechanical properties.

- **Chapter 5, Morphological induced improvements in the bulk mechanical properties of chemically etched additively manufactured Ti-6Al-4V micro-strut lattices:**

Chapter 5 examines post processing techniques which can minimise some of the aforementioned defects. Here, a chemical etching process is adopted for minimisation of surface roughness, and morphological defects inherited from the fabrication process. Following etching, potential improvements in mechanical properties are characterised.

- **Chapter 6, Chemical etching of additively manufactured Ti-6Al-4V biomaterials enhances mesenchymal stromal cell mineralisation:**

Having established a suitable process for chemically etching Ti-6Al-4V, which can effectively minimise topological defects, the next step is to examine the implications of using this approach for biomedical implants. Consequently, in Chapter 6, we explored the response of bone marrow derived mesenchymal stromal cells to chemically etched surfaces versus as-built surfaces.

- **Chapter 7, Conclusion and future work:**

Chapter 7 highlights the main findings and conclusions from this work, as well including a discussion of possible future work.

Chapter 2: Literature Review

2.1 Bone

2.1.1 Function and anatomy

Constituting the primary load-bearing component of vertebrate endoskeletons, bone tissue serves a variety of functions within the body [27]. Collectively forming the skeletal system, bone tissue contributes to body structure, and allowing for coordinated movement by providing a framework that muscles pull on as they work. Beyond a mechanical function, bone tissue also acts as a protective barrier, physically shielding internal organs and tissues.

In humans, the adult skeletal is comprised of 206 extraskeletal bones, and can be generally categorized into flat bones, and long-bones [28]. Generally, flat bones function for protection or muscular attachment, while long bones are load-bearing, and essential to skeletal mobility.

2.1.2 Composition and organization

Bones are lightweight to allow for efficient movement, yet also exhibit high strength, ensuring support and rigidity of the skeleton. The balance between these characteristics can be attributed to the hierarchical composite structure of bone (Fig 2.01) [29]. On a nanoscale, this structure is comprised of two primary phases: a mineralised phase, and an organic phase [29], [30]. The mineralised phase is primarily comprised of hydroxyapatite and contributes to hardness and rigidity. In contrast, the organic phase is comprised of proteins such as collagen and fibronectin, creating a flexible and resilient framework, allowing bones to resist stretching and bending.

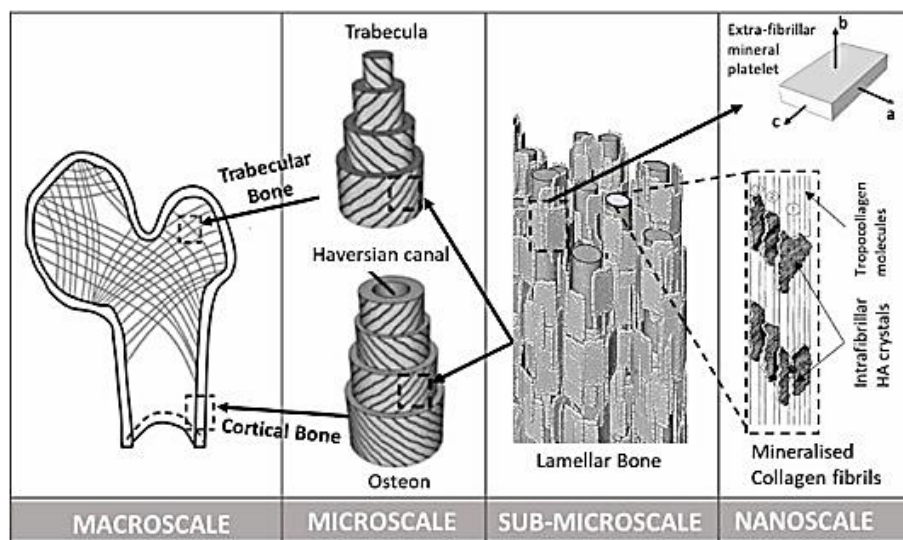


Figure 2.01. **Hierarchical structure of bone**, denoting the composite structure from macroscale (tissue level) to nanoscale (constitute level) [29].

On a larger length scale, bone is organized into two different types of tissue; cortical and trabecular (Fig 2.01) [29], [30]. Cortical bone constitutes the dense outer layer of bones, providing strength and stiffness, and is characterized by a solid structure comprised of functional units known as osteons. In contrast, trabecular bone is located closer to the interior, and characterized by a lattice-like network of thin trabeculae, absorbing shock and distributing forces[29]. Depending on the skeletal site, cortical and trabecular tissues are present in different ratios, ensuring a balance of strength and flexibility that caters to different mechanical and biological needs.

2.1.3 Cell types and functions

Bone is a dynamic tissue, continually adapting its structure in response to mechanical stresses. This behaviour is underpinned by a coordinated effort among various cell types in maintaining a balance between bone absorption and bone remodelling [31]. These cells are derived from either an osteogenic lineage (osteoblasts and osteocytes), or a monocyte-macrophage lineage (osteocytes) (Fig 2.02) [31].

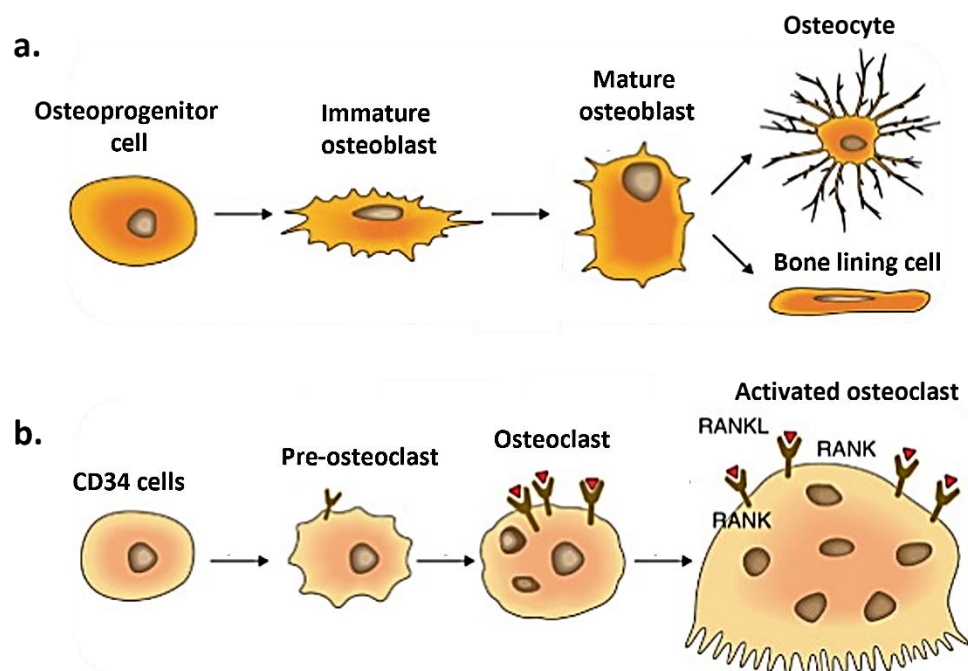


Figure 2.02. **Differentiation of bone progenitor cells**. Differentiation of a.) of osteoblasts, and osteoclasts along the osteogenic lineage, and c.) of osteoclasts along the osteoclastic lineage [31].

Osteoblasts are derived from the differentiation of osteoprogenitor cells along the osteogenic lineage, and are largely responsible for the ongoing development of new bone [32], [33], [34], [35] [32], [33], [34], [35] (Fig 2.02.a). Derived from mesenchymal stromal

cells (MSCs), osteoprogenitor cells represent a committed stage in the differentiation process. In the early stages of maturation, osteoblasts begin to secrete osteoid, an unmineralized organic matrix comprised of collagen type 1, and non-collagenous proteins [32], [35]. Subsequently, mineralisation occurs through the growth of hydroxyapatite nanocrystals within the osteoid; a process driven by the concentration of calcium and phosphate ions [33].

Further along the pathway of osteogenic differentiation, and in the absence of apoptosis, osteoblasts generally differentiate into either bone lining cells or osteocytes [31], [36]. Bone lining cells mark a period of inactivity, forming a layer on the bone surface. Although they do not actively contribute to the development of new bone during this period, they remain sensitive to mechanical and biochemical stimuli, allowing them to transition into active osteoblasts on demand. On the contrary, osteocytes are terminally differentiated, with little dynamic ability to return to active osteoblasts [31], [36]. The transformation of osteoblasts into osteocytes is denoted by osteocytogenesis, and is triggered by encapsulation within the secreted osteoid. Following this, they begin to adopt a stellate morphology, interconnected throughout the tissue by the cytoplasmic extension of numerous dendritic protrusions; facilitating the cells pivotal role in orchestrating cellular processes and bone remodelling across the tissue [34], [37].

Finally, osteoclasts are responsible for reabsorbing damaged or aged bone matrix. Separately, they are derived from the differentiation of mononuclear precursor cells along a monocyte-macrophage lineage (Fig 2.02.b) [31], [38].

2.1.4 Bone development

Bone development is a dynamic process initiated during early fetal development, and continues throughout adulthood in response to mechanical and biochemical stimuli. This occurs through two distinct mechanisms; intramembranous ossification and endochondral ossification [38], [39].

2.1.4.1 Intramembranous ossification

Intramembranous ossification revolves around the direct differentiation of MSCs along the osteogenic lineage, and is responsible for the development of all flat bones such as the skull and clavicle [39]. This process begins with the condensation of MSCs into a cellular aggregate. This is followed by differentiation along the osteogenic pathway into osteoprogenitor cells, and subsequently osteoblasts. As these cells mature, they begin to secrete osteoid, an unmineralized matrix primarily composed of collagen type 1, and non-collagenous proteins [32], [35]. Following this, mineralization of the osteoid occurs

through the concentration of calcium and phosphate ions, and consequent growth of hydroxyapatite nanocrystals within the matrix vesicles. During this process some osteoblasts become embedded in the newly formed matrix, and begin to form interconnecting cellular processes and eventually osteocytes. On the contrary, osteoblasts on the periphery begin to form a periosteum, and further growth occurs beginning with the condensation of MSCs.

2.1.4.2 Endochondral ossification

Endochondral ossification revolves around the formation of a hypertrophic cartilage template, which calcifies, and is remodeled into bone [38] (Fig 2.03). This method of ossification is most commonly seen during early fetal development, and responsible for the maturation of long bones, such as the femur [39].

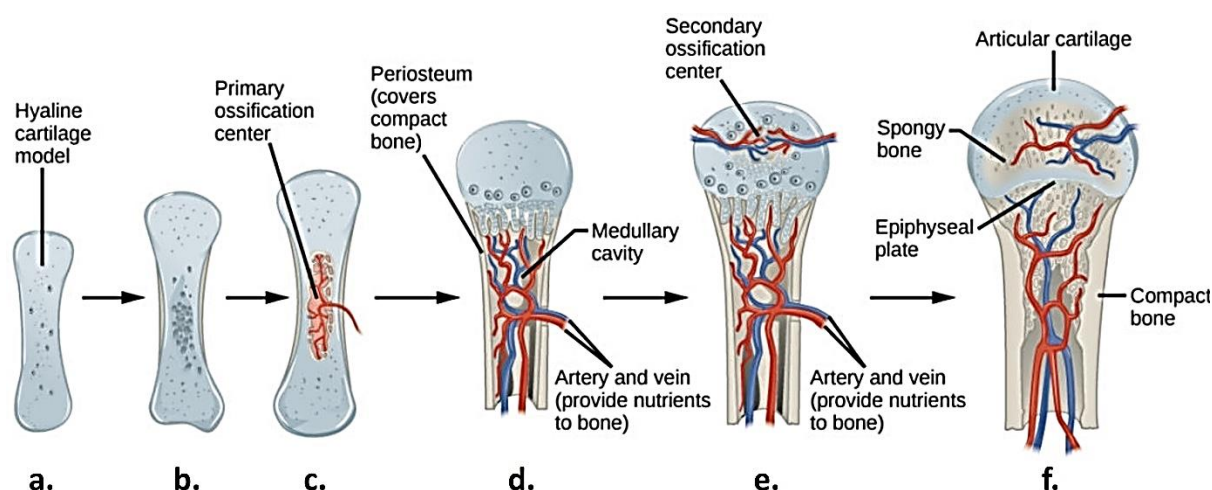


Figure 2.03. Endochondral Ossification. (a) Formation of the cartilage template, (b) Chondrocytes become hypertrophic, and the matrix is mineralised, (c) Blood vessels invade, and a primary ossification centre is formed, (d) Chondrocytes continue to proliferate at the epiphysis, (e) The secondary ossification centre is formed, (f) A layer of articular cartilage remains at the joint surface [38].

During this process, an early hyaline cartilage model is established through the condensation and eventual differentiation of MSCs into chondrocytes (CC) [38] (Fig 2.03.a). In turn, these cells begin to lay down the basis of the cartilaginous template, by secretion of extracellular matrix (ECM). After continued growth, CCs in the centre of the template stop proliferating and begin to undergo hypertrophy, and subsequently direct mineralization and eventually vascularisation of the surrounding matrix (Fig 2.03.b and Fig 2.03.c). Following this, the invasion of osteoprogenitor cells form the primary ossification centre at the diaphysis (Fig 2.03.c). During this process, cartilage continues to grow at the epiphyses (Fig 2.03.d). Subsequently, a secondary ossification centre eventually forms, where again, CCs stop proliferating, become hypertrophic, and result in

the influx of blood vessels and osteoprogenitor cells (Fig 2.03.e). Furthermore, any further bone growth occurs within the secondary ossification centre, and is governed by the epiphyseal plate, which continues to produce new cartilage that is replaced by bone, thereby facilitating bone lengthening. In adulthood, the end of skeletal growth is signalled when the CCs stop proliferating, and the epiphyseal plate is entirely replaced by bone [38], [40]. A layer of stable articular cartilage persists at the distal end of the epiphysis (Fig 2.03.f). CCs in this zone have a distinct origin from the more transient CCs involved in ossification. They are derived from a subset of cells, separated from the cartilaginous model at early developmental stages, and remain immune to hypertrophy and do not take part in the process of endochondral ossification [40].

2.1.5 Adaptive remodeling

Bone is a dynamic tissue, continually adapting its shape and microstructural architecture through processes known as modelling and remodelling [6]. Bone modelling is a continual process of bone adapting its structure in response to mechanical stimuli. During this process, the bone resorption activity performed by osteoclasts, and the bone formation activity performed by osteoblasts, are coordinated in a manner to adapt the bone such that its shape and structure are altered. Contrarily, bone remodelling is a process of continual renewal and repair of bone tissue over the course of a lifetime. This process is divided into four successive phases; Activation, Resorption, Reverse and Formation [6].

Activation: During the activation phase of bone remodelling, mechanical loading is sensed by the osteocytes via mechanotransduction, and subsequently activation of the bone lining cells is signalled [6]. In turn, osteoblast expression of Receptor Activator of Nuclear (RANKL) interacts with the RANK receptor expressed by pre-osteoclasts, and signals the differentiation into osteoclasts.

Resorption: The polarised osteoclasts attach to the underlying bone matrix and begin to reabsorb the tissue [6]. During this process, osteoclasts secrete hydrogen ions and the cathepsin K enzyme, which dissolve the mineralised component of the bone matrix, and digests the protein matrix respectfully. Following this, osteoclasts undergo apoptosis.

Reverse: A transitional phase, involving the removal of debris and preparation of the resorption site for new bone formation [6].

Formation: Osteoblasts are recruited to the reabsorbed area following the release of several growth factors during the resorption phase, including Bone morphogenic Protein (BMP) and Transforming Growth Factor - β (TGF- β). Following this, the osteoblasts begin

to lay down the osteoid, which is subsequently mineralised through concentration of calcium and phosphate ions [32], [35].

2.1.6 Fracture healing

Despite undergoing continued renewal and repair, traumatic injuries or pathological conditions can lead to bone fracture. Fortunately, bone fracture can also be repaired through a process known as fracture healing [1]. When the bone breaks, blood vessels and the surrounding tissue are torn and haemorrhage. Coagulation of subsequent bleeding leads to the formation of a haematoma, which encloses the injury site. As a result of a subsequent inflammatory response, fibroblasts and endothelial cells are recruited to the injury site, leading to angiogenesis and the formation of granulation tissue. As MSCs are differentiated along a chondrogenic pathway, this tissue is gradually replaced by a fibrocartilage callus [6], [41]. The centre of this callus is gradually replaced by woven bone through the process of endochondral ossification, while the exterior gradually forms a periosteum through the process of intramembranous ossification. Over time, the newly formed woven bone is remodelled into mature laminar bone, and the vascular supply is reorganised in response to the developing bone tissue.

2.1.7 Clinical strategies for bone repair

Despite this inherent capacity for self-repair, a number of situations may arise in which bone will not heal naturally over the course of a lifetime. For instance, in bone defects above a critical size, bridging will not occur [1]. Such defects are referred to as critically sized defects, and in such instances, clinical strategies may be required to support and stabilize the bone, or to enable full healing. Circumstances may also arise where a pathologic non-healing segment of bone may need to be removed. For example, later stages of osteoarthritis may progress into the underlying layer of subchondral bone, and will not heal naturally [42].

Among these clinical strategies, the most commonly used approach for bone repair is by transplanting a bone graft [1]. In this case, the optimal choice is an autograft, taken from the patient's own tissue. However, a significant disadvantage of this approach is donor site morbidity. Furthermore, due to limitations of the volume of bone which can be harvested, this approach is only suitable for repairing small areas. Consequently, an alternative choice is the use of allografts taken from a cadaver, or xenografts, taken from an animal source. These approaches have their own disadvantages, particularly revolving around difficulties with osteointegration, and the potential for an immunogenic response [3].

Bone tissue engineering aims to introduce new functional synthetic bone grafts, typically in the form of a scaffold [2], [3]. Engineered scaffolds have great potential for bone repair, while also circumventing many of the problems associated with autografts or xenografts. Depending on the method of fabrication, engineered scaffolds may also allow for an enhanced level of customisation, which would be otherwise unachievable by traditional bone grafting [6]. This level of freedom allows for a more tailored design, more suitable to complex defect morphologies, as well as potentially imparting enhanced functionality. Consequently, bone tissue engineering has the potential to fully replace the conventionally used bone graft. At a minimum, the engineered scaffold should allow for bone ingrowth, while also maintaining structural stability for the requisite duration [6]. In light of these factors, there is a continuing effort to identify biomimetic materials and structures that are more suitable for skeletal repair [4], [5], [7].

As discussed through this section, both traditional bone grafts and tissue engineered scaffolds play an essential role in treating defects of a critical size, that would not otherwise heal by themselves. In either case, the mechanism of healing is similar to the mechanism of fracture healing, discussed in Section 2.1.6. After implantation, an inflammatory response is triggered, which ultimately leads to hematoma formation. Subsequently, MSCs are recruited to the surface of the implant, and begin to differentiate along an osteogenic pathway through the process of contact osteogenesis [6], [41]. This results in the formation of new immature woven bone on the implant surface. Alongside this, bone formation also occurs through distance osteogenesis, characterised by new bone growth from the surrounding tissue, towards the implant surface [6], [41]. In either case, the newly laid bone gradually fills the gaps between the implant and the surrounding tissue. Subsequently, this bone is remodelled into mature laminar bone, resulting in complete osteointegration with the surrounding tissue.

2.1.7.7 Metallic biomaterials

As discussed in Section 2.1.7, the potential advantages of tissue engineered scaffolds has driven a continued effort to identify biomimetic materials more suitable for skeletal repair. Among these materials, titanium and its alloys have emerged as a favorable option for osteo-integrated bone implants [4], [5]. From a long history of application in medical devices, it is well established that titanium is biocompatible. The overall success of the implant is heavily dependent on this characteristic. Broadly, the biocompatibility of materials used for orthopedic implants can be classified as cytotoxic, which may illicit tissue damage or implant rejection; bioinert, showing minimal interaction with the surrounding tissue, yet allowing new bone growth via distance or contact osteogenesis; or bioactive, typically involving the formation of a chemical connection between the material

and surrounding tissue [5]. Titanium falls into the category of a bioinert material. This is largely a consequence of an inherent formation of a surface oxide film, separating the metal from the environment. This passive layer exhibits chemical stability, and is minimally reactive with the surrounding tissue [2], [5]. Consequently, in addition to exhibiting bioinert characteristics, titanium alloys also exhibit excellent corrosion resistance. Despite the advantages of these attributes in an *in vivo* setting, the limited interaction between the implant and surrounding tissue may prolong healing compared to bioactive materials. These materials typically contain Ca and/or P groups, and may promote osteointegration of the implant via bonding osteogenesis; by facilitating the growth of a hydroxyapatite surface layer [5]. However, these materials are often lacking in other desirable qualities, such as mechanical properties. The biocompatibility of titanium alloys, on the other hand, is coupled with a mechanical behaviour close to that of long bones. This extends to a high strength to weight ratio, which in long bones facilitates efficient movement, yet also skeletal rigidity [4], [5]. Titanium alloys also exhibit a relatively low elastic modulus, and may limit stress shielding. In other materials, the stiffness gradients of the implant may limit mechanical stress in the surrounding tissue, and lead to more significant stress shielding. This occurs in response to bones' dynamic ability to remodel to local stresses, which in this case leads to bone resorption. Although the low stiffness of titanium alloys may limit these effects, its elastic modulus is higher than bone, and some stress shielding may still occur [4].

2.1.7.2 Design by additive manufacturing

Additive manufacturing techniques have enabled the fabrication of geometrically complex porous lattice structures, and as such have been widely adopted for orthopaedic implants and bone-tissue engineering applications [11], [43]. When applied to orthopaedic implants, these lattices can offer many advantages over traditional non-porous implants. This extends to allowing tissue ingrowth and more closely recapitulating the stiffness of the native tissue [8], [9].

From a design perspective, the lattice is characterised as a topology ordered periodic structure, comprising of one or more repeating unit cells. Aspects of both the unit cell, and its connectivity within the lattice structure can be optimised as to achieve unique physical characteristics properties [8], [9], [44], [45]. Among these characteristics, mechanical properties are critical to the overall success of orthopaedic implants. In the most basic sense, these properties determine structural stability under loading, but also play a central role in bone growth and osteointegration, as such processes are regulated by the local mechanical environment through mechanotransduction.

Through the control of lattice design, mechanical properties can be tuned to closely recapitulate that of the native tissue. For trabecular bone, this is in the range of 0.05-2GPa, while cortical bone is in the range of 3-30GPa [8], [9], [44], [46], [47]. Although a large number of design variants may meet these requirements, additional demands of supporting bone growth and osteointegration lead to a much smaller range of lattice designs suitable for biomedical applications [45]. A minimum lattice porosity is also necessary to allow cell migration and nutrient exchange, while an excessive level of porosity can bring its own problems, including slow proliferation. In general, lattice porosity in the range of 50-90% is considered optimal for osteointegration [8], [45], [48]. Consequently, lattice design for biomedical applications typically require a delicate balance between ensuring sufficient implant strength and stiffness, but a low volume fill fraction to impart porosity. Only a narrow range of lattice designs meet all these requirements [8], [44], [45], [48].

2.2 Selective laser melting

2.2.1 Basic process

Selective laser melting (SLM) is regarded as a powder bed fusion process, whereby a laser beam is used to selectively melt areas of a metallic powder bed into a liquid melt-pool, which solidifies and cools rapidly [49]. For each build layer, the laser traces a predefined scan path representing a cross-section of the design. Once a build layer has been scanned, the build platform is lowered by a predefined layer thickness and a new layer of powder is deposited. The process is repeated until each layer of the build has been completed.

Most commonly, a contour-and-hatch scanning strategy is adopted for processing each layer of the build (Fig 2.04) [50]. In this approach each layer is processed by the laser with an outer scan, which traces the contour boundary of the CAD geometry (Contour Scan). To achieve agreement between the as-designed, and as-fabricated geometries, the counter scan is typically offset from the CAD boundary, accounting for the thickness of the melt pool. Following the contour scan, the enclosed area is processed by laser with inner scans, tracing a hatching pattern (Hatch Scan).

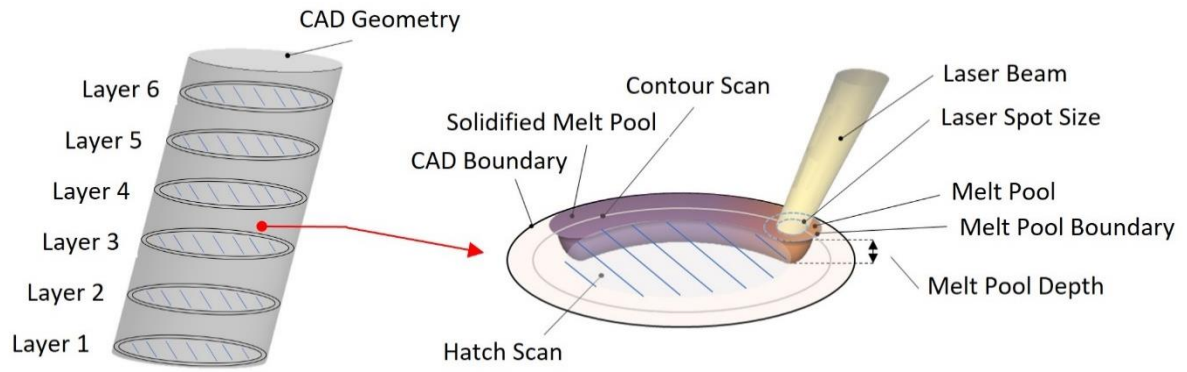


Figure 2.04. **Contour-and-hatch scanning strategy.** In the contour-and-hatch scanning strategy, each layer of the CAD geometry is processed by an outer contour scan. The enclosed area is then processed by inner hatch scans.

2.2.2 Process inherited defects

2.2.2.1 Porosity

During SLM processing, printing parameters are generally optimized in order to maximize density [51], [52], [53]. It is well accepted that the stability and dimensions of melt pool largely drive the extent of porosity. In turn, it can be deduced that processing parameters including laser power, scanning speed, and spot size, which have the greatest effect on the melt pool, will have a significant influence on porosity [49]. However, for full density, it is also essential that the scanning strategy and layer thickness are appropriate to allow for complete melting, and consolidation of the powder material. Consequently, hatch distance in the case of the C&H scanning strategy, as well as layer thickness, also play an important role in the determination of the final porosity. Practically, these parameters are characterized by the energy density function, which describes the energy density input per unit volume of material. In the most basic sense, this must be high enough to sufficiently melt the material, but also low enough to avoid melt pool instability [49], [51], [52].

Below the critical threshold for unstable melt pool dynamics, melt pool formation is dominated by the conduction mode of heat transfer into the surrounding material. However, the Marangoni effect also plays an important role, governing fluid flow within the melt pool, and consequently heat transfer by convection. In SLM processing, Marangoni flow of the molten material is induced by surface tension gradients within the melt pool. As a result, fluid flow occurs from areas of low surface tension towards areas of higher surface tension. As surface tension typically reduces with temperature, this generally prompts a radial outward flow, producing a wider, and shallower melt pool [54]. At the same time, spreading is also constrained by inertial and viscous forces [55].

Balling is a type of defect inherited through SLM fabrication when the melt pool can not wet the underlying substrate [49], [55]. During this process, the continuous melt pool track breaks up into discrete spherical droplets (Fig 2.05) [56]. Consequently, the deposition of following layers is impeded, resulting in porosity. More commonly, balling occurs at low energy densities, where lower temperature gradients may result in higher dynamic viscosity [55]. Subsequently, these conditions may impede proper spreading, resulting in high contact angles between the melt pool and the underlying substrate. Following this, balling may occur as a result of capillary instability, which transpires in order to minimize the surface free energy [55].

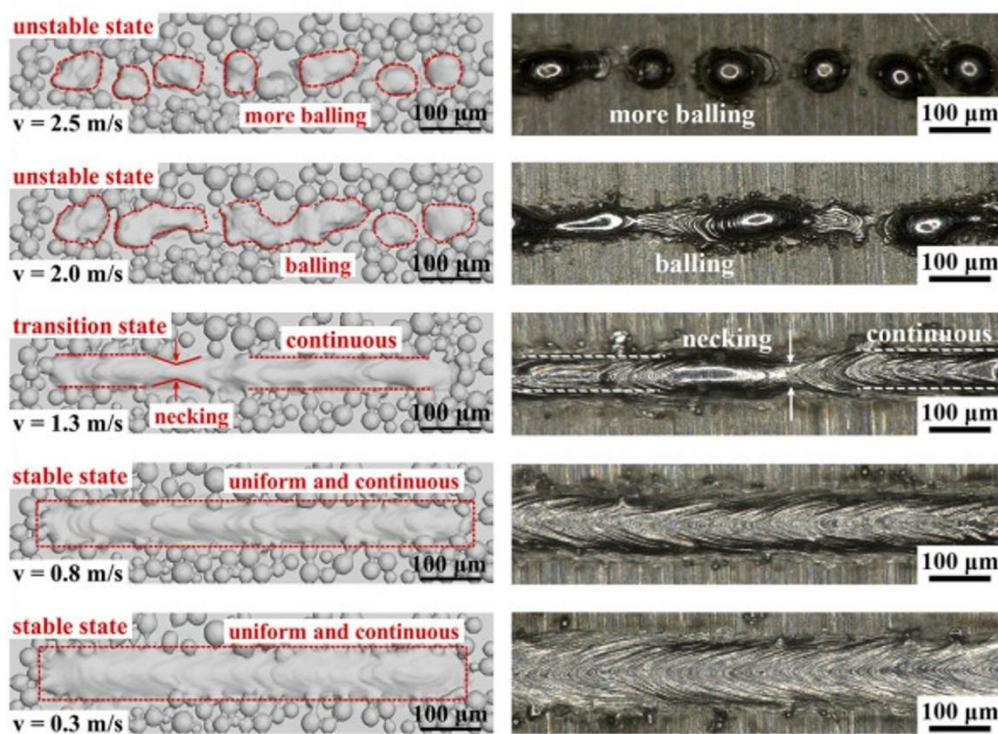


Figure 2.05. **Balling defects.** Balling occurs when the continuous melt pool track (bottom) breaks up into discrete spherical droplets (top) [56].

More common than balling, is the inheritance of lack of fusion defects (LoF) [52]. The occurrence of these defects arises when the powder is not completely melted or does not fuse to the underlying substrate. Consequently, these defects are associated with lower energy density inputs [51], [52], [57]. In general, these defects may arise in two distinct circumstances [58]. Under the first circumstance, LoF defects may occur from incomplete melting of the metal powder. This occurs at low energy density inputs, which result in a small melt pool size relative to the hatch distance, and the layer thickness. Relative to hatch distance, this may result in the entrapment of un-melted powder between scan tracks due to insufficient overlap. Relative to layer thickness, due to insufficient penetration depths,

this may result in an island like structure, unfused to the previous layer. As a result of these effects, LoF defects are typically distributed perpendicularly to the build direction. Moreover, the subsequently rougher surface contributes to the second circumstance in which LoF defects may arise. Here, the rough surface directly contributes to uneven layer thickness, and to the poor flow of molten material. This may lead to the formation of LoF defects in successive layers.

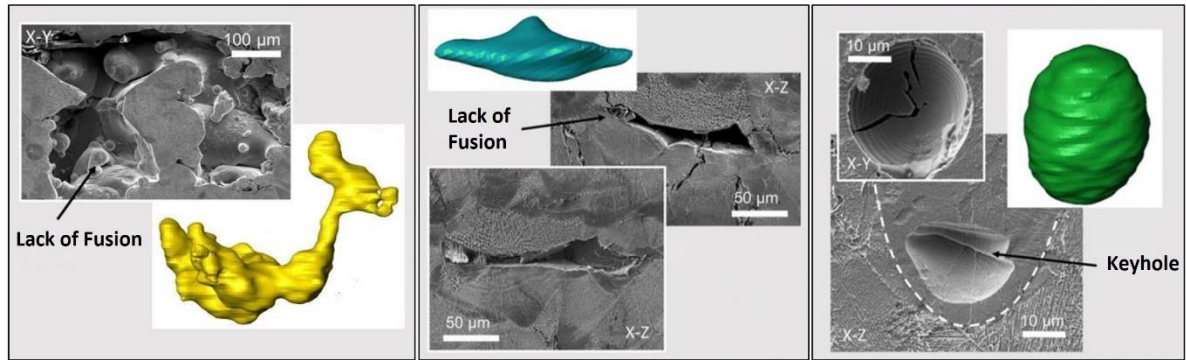


Figure 2.06. **Porous defects inherited through SLM fabrication.** SEM images and reconstructed μ CT models, showing typical morphology of lack of fusion defects (left and middle), and keyhole defects (right) [59].

On the contrary, too high an energy density input may also impart porosity, typically categorized by gas entrapment or keyhole type defects. These defects are largely a consequence of unstable melt pool dynamics (Fig 2.06) [51], [52], [60]. At excessive energy density inputs, the intensity of the laser is high enough so that recoil pressure becomes significant. In turn, this leads to the formation of a keyhole like depression. Under recoil pressure, the melted material at the base of the depression is ejected upwards, and subsequently collapses back in on itself (Fig 2.07). This leads to a vortex forming, driving lateral expansion in the uppermost part of the depression. As the laser moves on, the recoil pressure is subsided and material flows back into the depression, and solidifies. However, if the depression is deep enough, an unstable inward collapse may occur, leaving gas entrapment and keyhole type defects at the base of the depression, as the material solidifies.

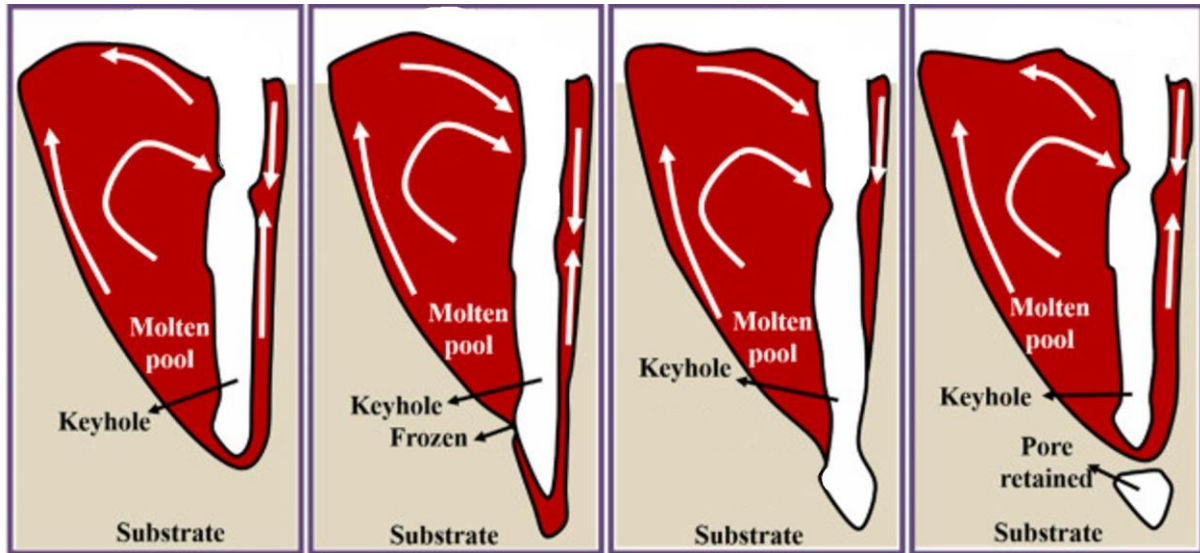


Figure 2.07. **Schematic depicting the evolution of keyhole type defects.** At high energy density inputs, recoil pressure leads to the formation of a keyhole like depression. Molten material at the base of the depression is ejected upwards, which subsequently collapses in on itself. This gives rise vortex formation, which leads to lateral expansion of the upper section of the depression. As the laser moves on, an unstable collapse occurs, leaving keyhole porous defect at the base of the depression as the material solidifies [60].

As discussed throughout this section, porosity may occur when the energy density input is excessively low, or excessively high. Consequently, the optimal energy density can be found somewhere in the middle [49], [51], [52], [61]. Although the porosity can be minimised by the appropriate selection of processing parameters, some level of porosity is very difficult to avoid. As discussed in Section 2.2.3.1, among the aforementioned defect types, LoF pores are much more detrimental to mechanical properties. Consequently, slightly higher energy densities are often favoured, even at the sacrifice of small amounts of gas entrapment or keyhole type defects [61].

2.2.2.2 Surface roughness

The surface roughness of SLM manufactured components is inherently rough. Moreover, the roughness of these components is largely dependent on the orientation of each surface relative to the build direction. Consequently, each surface can be broadly categorised as up-skin (upward facing), down-skin (downward facing), or side-skin (facing parallel to the build direction) [62], [63]. Of course, most surfaces lie somewhere in between, due to an inclined orientation between 0° and 90° .

The roughness of horizontal, up-skin facing surfaces is largely dependent on the defects mentioned in Section 2.2.2.1. For example, balling can lead to a significant increase in surface roughness. Consequently, the control of up-skin surface roughness may be at least somewhat controlled through parameter optimisation [62], [63]. The roughness of down-

skin, and side-skin surfaces is less controllable. Here, surface roughness is primarily a consequence of partially adhered powder [63], [64]. However, due to the physics of melt-pool, along with powder size and morphology, these defects are largely unavoidable [64]. Despite this, certain geometrical and processing conditions may lead to higher amounts of partially adhered powder on the surface. Such conditions may arise on down-skin facing surfaces. Here, molten material more easily flows downwards by gravity and the capillary effect. As a result, the molten material flows into voids in the underlying powder bed, resulting in much more partially adhered powder [65]. Additionally, such effects may be more pronounced at higher energy density inputs, when heat accumulation more effectively infiltrates the surrounding area, resulting in the partial melting of higher amounts of partially adhered powder [63], [65]. As a result, these effects are often minimised using a lower energy density input in the contour scan, compared to the inner hatching scans.

Up-skin and down-skin inclined surfaces also exhibit a staircase effect (Fig 2.08). This is apparent as a layer-wise, staircase pattern, and a consequence of attempting to represent inclined or curved surfaces by rectilinear steps [63]. On the up-skin surface, these effects are simply apparent as a stair-case pattern, with partially melted powder adhered to the step edges [66]. On the down-skin surface, a higher roughness is typically observed, largely a consequence of the underlying powder on overhang sections [63].

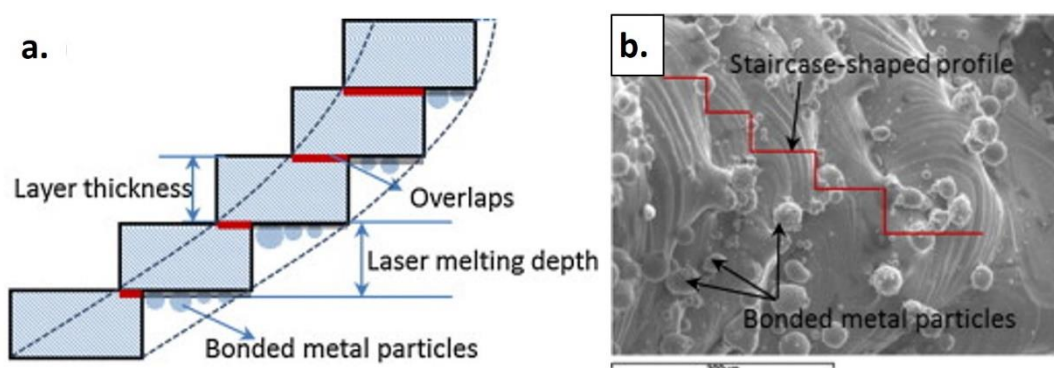


Figure 2.08. **The staircase effect.** A layer-wise, staircase pattern, may arise as consequence of attempting to represent inclined or curved surfaces by rectilinear steps. Showing a.) a schematic of this effect, and b.) an SEM micrograph of the up-skin surface [67].

2.2.2.3 Design inherited defects

Component design plays an important role in the determination of surface roughness, but also manufacturability. As discussed in Section 2.1.7.3, AM techniques such as SLM have enabled the fabrication of geometrically complex porous metallic lattice structures. Such structures can be typically characterised as an interconnected network of micro-strut

building blocks. As a consequence of the factors discussed in Section 2.2.2.2, the orientation of these struts relative to the build direction plays a significant role in the determination of surface roughness. For example, greater inclination angles may result in a much rougher down-skin surface as a result of the effects mentioned previously. However, a number of other effects also have a significant impact on the manufacturability of lattice structures. In a completed build, each strut is typically suspended between two nodes. However, during fabrication, struts evolve as cantilever beams [68]. Without sufficient supports, excessively long overhangs may become susceptible to structural distortion [68], [69], [70]. This largely occurs as a result of the poor heat dissipation into the underlying power bed. Temperature gradients arise, which result in the upward bending of the printed layer (Fig 2.09) [70]. These effects are more apparent as the overhang length is increased. Consequently, at a certain point bending may exceed that of the layer thickness, ultimately disrupting re-coater spreading of subsequent layers, and increasing the likelihood of print failure. Strut diameter and inclination angle also play a significant role in these effects [68], [70]. As strut diameter is increased, the material becomes stiffer and offers more resistance to bending [70]. As inclination angle is reduced (relative to the vertical), the unsupported overhang length is reduced, effectively alleviating these effects [70].

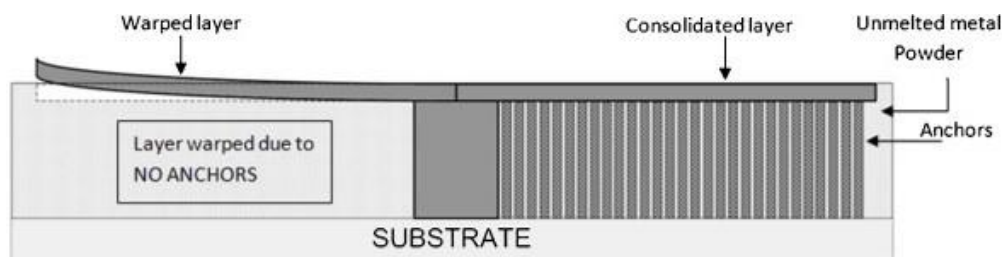


*Figure 2.09. **Overhang regions are prone to warping.** When the inclination angle is high (relative to the build direction), temperature gradients arise due to poor heat dissipation into the supporting powder bed, and result in the upward bending of the printed layer. The addition of supports may alleviate these effects [70].*

In addition to driving surface roughness, surface defects also impede the near-net-shape manufacturability of SLM fabricated components [71], [72], [73], [74]. This is particularly important in micro strut lattices, due to a disproportionate inheritance of such defects. This occurs due to an increase in the surface-to-volume ratio of small diameter struts. As a result, surface defects account for a much larger portion of the total material volume in micro struts, compared to traditional bulk sized components. These effects result in a new class of irregularity in small diameter struts, which can be described as morphological. In general, morphological irregularities can be characterised by deviations between the as-designed and the as-fabricated geometries (Fig 2.10). In the most basic sense, this extends

to strut oversizing, which is simply a consequence of partially adhered powder extending beyond the CAD boundary [73]. However, due to the resulting non-homogenous surface, large variations in strut cross-section may also arise [72], [73]. Subsequently, waviness may also occur, which is characterised by the misalignment of the centroid of each cross-section from the centroidal axis of the strut [73]. The extent of these effects is largely influenced by strut diameter. In smaller diameter struts, surface defects represent a much larger portion of the total material volume, consequently leading to larger deviations between designed and fabricated geometries. However, build orientation also plays a significant role. Inclined surfaces may result in much more partially adhered powder on the down-skin surface, compared to the up-skin surface. These effects largely contribute to the transition from an as-designed cylindrical profile to a more elliptical-like profile [71], [74].

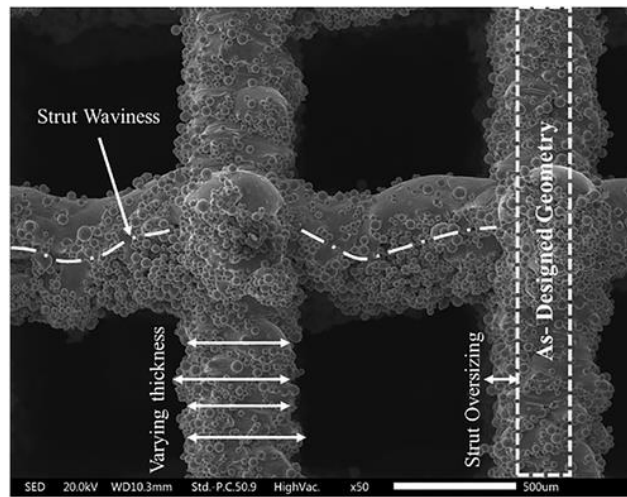


Figure 2.10. **Morphological Defects.** In addition to surface roughness, morphological irregularities may also arise in small diameter struts. These irregularities arise as largely a consequence of the large portion of the total material volume that is accounted for by surface defects [73].

It is important to note that deviations between the as-designed and as-fabricated geometries will also extend beyond that of the micro-strut building blocks. For example, variations in strut diameter will also extend to pore size [75]. This is particularly important for biomedical applications, where the pore size to tightly controlled in order to regulate biological process necessary for osteointegration, including vascularisation and cell proliferation.

2.2.2.4 Computational modelling

As discussed in Section 2.2.2.1 to 2.2.2.3, processing of the powder material plays an important role in determining the inheritance of defects from PBF. Computational

modelling is often used as a tool to study this process and ultimately for the prediction of defects for different processing parameters, or across different geometries.

Using this computational modelling, laser processing of the powder material is typically characterized by a Gaussian heat flux [76], [77]. In the most basic sense, the thermal histories during this process can be considered by the transient heat conduction equation, described as follows.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + q''(x, z)$$

Eq. 1

Where; ρ is density (kg/m^3), C_p is heat capacity ($\text{J}/\text{kg}/\text{K}$), and k is thermal conductivity ($\text{W}/\text{m}/\text{K}$).

The total heat flux $q''(x, z)$, can be described by considering the heat input imposed by the laser, and the heat losses as a result of convection and radiation. The heat input imposed by the laser is typically considered by either a surface or a body Gaussian heat flux, which traces the scanning pattern as follows.

$$q''_{\text{surface}}(x, z) = \frac{2AP}{\pi r_0^2} \exp \left(\frac{-2((x-x_0)^2 + (z-vt)^2)}{r_0^2} \right)$$

Eq. 2

$$q''_{\text{body}}(x, z) = \frac{4\sqrt{2}AP}{\pi\sqrt{\pi}r_0^3} \exp \left(\frac{-2((x-x_0)^2 + (z-vt)^2)}{r_0^2} \right)$$

Eq. 3

Where; A is absorptivity, P is power (W), r_0 is laser radius (m), and v is the scanning velocity (m/s).

Alongside the heat input, heat losses from convection and radiation are considered as follows.

$$q''_{\text{loss}} = h(T - T_{\text{sur}}) + \varepsilon\sigma(T^4 - T_{\text{sur}}^4)$$

Eq. 4

Where; h is the heat transfer coefficient ($\text{W}/\text{m}^2/\text{K}$), ε is emissivity, σ is the Stefan-Boltzmann constant ($\text{W}/\text{m}^2/\text{K}^4$), and T_{sur} is the surrounding temperature (K).

It is important to note that although this approach of modelling thermal histories has proved effective in many studies [76]. As discussed in Section 2.2.2.1, consideration of solely the heat conduction equation is a simplification of the problem, which ignores the effects of fluid flow within the melt pool. Fluid mechanics models may also incorporate these effects, which at the most basic level may be described by the Navier-Stokes equations [77].

2.2.3 Mechanical properties

2.2.3.1 Porosity

Defects inherited from the fabrication process are well understood to have a detrimental effect on mechanical properties [51], [52]. Among these defects, internal porosity is particularly detrimental. These effects are typically apparent under tensile loading, rather than compressive, due to the inherent opening of pores rather than the closing of them. Experimentally, this extends to both the quasi-static tensile test, and dynamic tension-based fatigue loading regimes [19], [78]. Under quasi-static tensile loading, deformation occurs in a material which up to the yield point is characterised by an elastic behaviour [79]. This behaviour is often described by the elastic modulus, which describes a linear relationship between stress and strain, and by essence stiffness. The elastic modulus is largely material dependent, however independently, an increase in porosity can be generally correlated to a reduction in stiffness. This can be largely attributed to the amount of material in any given cross-section that is load bearing. This is reduced by porosity, and consequently leads to a reduction in the applied force at any given level of strain [80], [81]. This leads to a reduction in the average stress measured across the cross-section, and subsequently to an apparent reduction in the elastic modulus. Although these effects are largely correlated to the amount of porosity, the type of porosity also has a critical role to play. Generally, LoF pores have been reported to be far more detrimental compared to gas entrapment or keyhole type pores [81], [82]. These effects have been largely attributed to pore morphology. Relative to gas entrapment or keyhole type defects, LoF pores exhibit a much more elongated morphology, typically orientated perpendicular to the build direction. Consequently, if loading is orientated parallel to the build axis, these pores result in a much more significant reduction in the cross-sectional area compared to gas entrapment or keyhole type pores. Notably, these effects are not as apparent when loading is orientated perpendicular to the build axis, or at low levels of porosity, before the elongated morphology has evolved [83].

The yield point characterises the extent of elastic deformation, at which the material begins to plastically deform [79], [84]. As discussed in Section 2.2.5.3, this occurs when a critical stress, referred to as the yield stress, is exceeded, allowing plastic flow. Generally, an increase in porosity has been correlated to a reduction in the yield stress [51], [52]. In the most basic sense, this can be attributed to the same effects which drive a decrease in stiffness. Again, the reduction in load bearing material leads to a decrease in the applied force. This results in a decrease in the average stress, which is measured across a given cross-section, and consequently to an apparent reduction in yield strength. It is important to remember that this effect is not driving a lower critical stress in the bulk material at

which plastic deformation occurs. Rather, it is an apparent effect, from the calculation of stress across the entire cross-sectional area. Consequently, and similar to elastic modulus, these effects are more apparent for LoF pores compared to gas entrapment or keyhole type pores. Furthermore, in regard to material strength, the effects of LoF pores extend beyond a reduction in the amount of material that is load bearing. A number of studies have observed that the resultant drop in strength could not be entirely accounted for by the reduction in load bearing area [51], [52]. Rather, there is a combined effect, which also extends to the effect of stress concentrations around the irregular pore morphology. These effects are not as apparent for gas entrapment or keyhole type pores, due to their typically much more tapered and spherical morphology. In such cases, the reduction in strength has been directly correlated to the loss in load-bearing area. However, for LoF pores, the effects of stress concentrations are much more apparent. This is largely a consequence of their irregular pore morphology, which effectively acts as a crack under loading. Here, stress concentrations are largely determined by the major axis of the crack under loading, and the sharpness of the crack tip [51]. These effects result in a lower external applied force necessary for plastic flow, and consequentially in a reduction in strength.

After yielding, stress typically continues to increase up to the ultimate tensile strength (UTS) [84], [85]. This is largely a consequence of strain hardening, which is discussed further in Section 2.2.5.3. In ductile materials, failure typically occurs beyond the UTS, beginning with the process of micro-void nucleation. In general, failure begins at the centre of the sample due to a state of maximum triaxial stress [85], [86], [87]. These voids act as cracks, and failure subsequently progresses in the material through crack growth, and coalescence [88]. Consequently, this process is accelerated by existing pores inherited from the fabrication process. Generally, the ductility of this process is characterised by the elongation at fracture, and typically exhibits a much higher sensitivity to porosity compared to the elastic modulus or strength [51], [52]. This is largely driven by stress concentrations around the crack tip, which drive further crack growth [85]. As discussed throughout this section, both pore size and the sharpness of the crack tip play a dominant role in determining the local stress. Consequently, these effects are more apparent for LoF pores, on account of their more irregular morphology [51], [52]. Following crack growth, the next stage of failure is characterised by void coalescence. At early stages of failure, this typically occurs by local necking of the ligaments between voids (Fig 2.11.a) [87], [88]. These effects typically result in a dimpled fracture surface, normal to the direction of the applied load (Fig 2.11.b). With continued elongation, a large crack develops. As we have discussed, this generally occurs at the centre of the sample due a state of maximum triaxial stress. Ahead of the crack tip, a state of high stress leads to further void nucleation and growth, and the crack subsequently grows outwards [85]. As the crack nears the edge of

the sample, the free surface does not constrain plastic flow, leading a state of plane stress. As a result, a shear band develops, which is the favoured mechanism of deformation in ductile materials. [85], [87], [89]. This occurs along the axis of maximum shear stress, at a 45° degree inclination to the principal stress [80], [85], [87], [90], [91], [92]. Along the shear band, void coalescence occurs through the shearing of the ligaments between voids (Fig 2.11.c) [85]. This results in a unique fracture surface characterised by parabolic shear dimples (Fig 2.11.d).

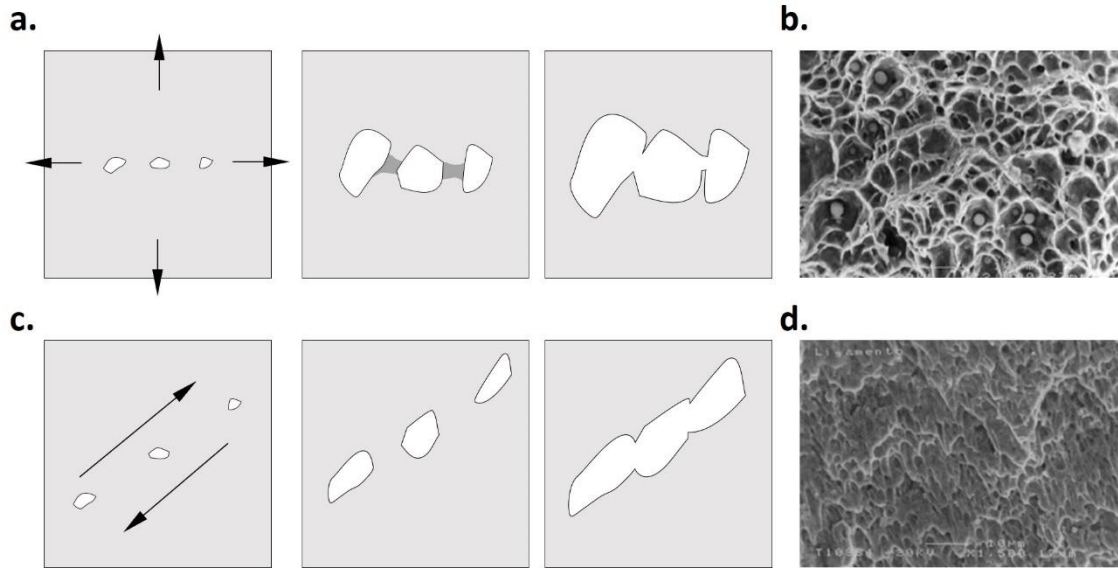


Figure 2.11. **Micro-void coalescence.** Micro voids may coalesce a.) by internal necking, resulting in b.) a dimpled fracture surface. c.) Alternatively, along a shear band, void coalescence occurs through the shearing of the ligaments between voids. d.) This results fracture surface characterised by parabolic shear dimples [93].

Fatigue is characterised by the progressive damage that occurs in a material that is subjected to cyclic loading [94]. This occurs through the initiation of a small crack, which gradually propagates through the material with each loading cycle. Eventually, a point is reached where stable crack growth can no longer be maintained, leading to catastrophic failure. This gives rise to three distinct zones in fatigue driven failure (Fig 2.12) [94], [95], [96]. Under the assumption of traditional linear elastic fracture mechanics (LEFM), a pre-existing sharp crack may give rise to subsequent fatigue mediated damage and crack propagation. Here, crack nucleation as well as early growth are considered by an initiation phase, often referred to as Zone I. This may arise as a result of microscopic defects in the material, when the stress intensity factor at the crack tip (K) exceeds a threshold value (K_{th}) [97], [98]. Beyond this point, energy levels are sufficient for crack tip opening, and the crack grows along the slip system of maximum resolved shear stress. This occurs on a length scale comparable to that of the local grain dimensions, and is consequently

associated with a rather tortuous pathway [99]. As the crack continues to grow beyond this point, K also begins to increase. Eventually, a point is reached when the plastic zone ahead of the crack tip has grown and covers multiple grains. As a result, further crack growth is associated with less sensitivity to microstructural discontinuities, and consequently, is associated with accelerated, yet stable crack propagation [99]. This phase of crack growth is often referred to as Zone II, and under the assumption of LEFM can be characterised by the Paris law [94], [97]. Continued crack growth in Zone II results in an increase in the stress intensity factor, until K approaches the critical stress intensity factor, K_c . This is often referred to as the fracture toughness and defines the material's ability to resist crack propagation [97], [98], [100]. Above K_c , there is a strong likelihood of entering Zone III, characterised by fast brittle catastrophic fracture.

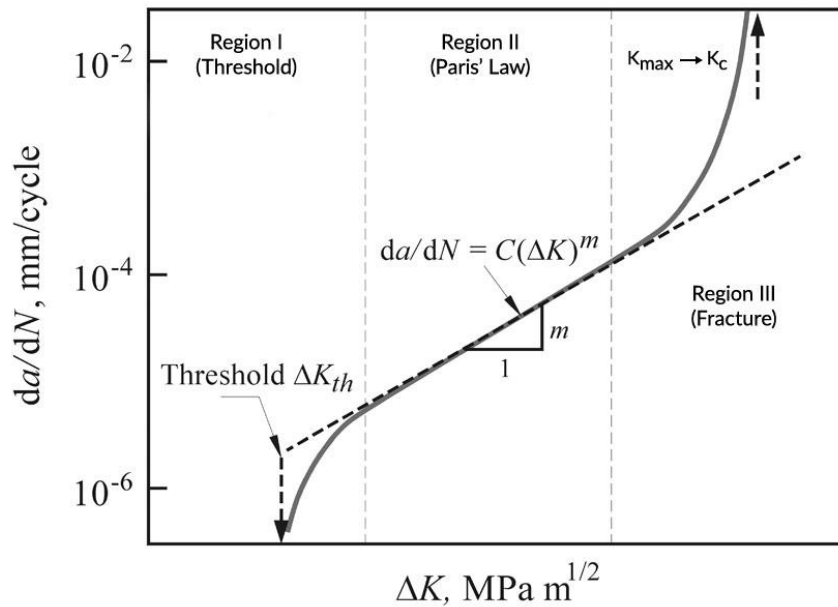


Figure 2.12. **Fatigue crack growth rate curve.** The fatigue crack growth rate can be plotted as a function of ΔK under the assumption of LEFM [95].

The applied far field stress will have a significant impact on the stress intensity factor [94], [98]. Rather intuitively, a larger applied stress will result in a larger maximum stress at the crack tip. Consequently, the size of each fatigue zone is largely dictated by the fatigue loading regime. In general, fatigue loading can be categorised across a spectrum, which ranges from low cycle fatigue (LCF) to high cycle fatigue (HCF). LCF involves relatively high stress cycles, nearing the materials yield strength [101], [102], [103]. As a result of these high stress cycles, the stress intensity factor at the crack tip arrives at K_c at a relatively small crack length. Consequently, stable crack growth can only be maintained for a relatively low number of cycles to failure, and results in a relatively small crack growth zone (Fig 2.13.a). On the contrary, HCF involves relatively lower stress cycles [101], [102].

As a result, a much larger crack length is required for the stress intensity factor to reach K_c . Subsequently, HCF is characterised by a much larger number of cycles to failure, and is accompanied by a much larger crack growth zone (Fig 2.13.b). At the far end of the HCF loading regime, the fatigue limit defines the theoretical stress at which fatigue failure will not occur. For practical purposes, this is generally defined by the stress at which the material can survive 10^7 loading cycles [104].

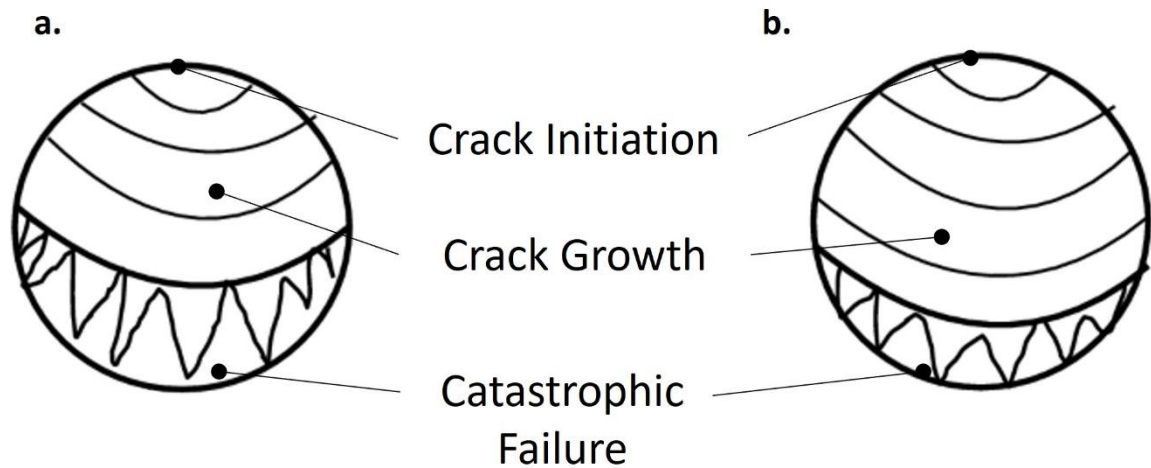


Figure 2.13. **Illustration of the fatigue fracture surface.** Fatigue fracture can be divided into three stages, namely, crack initiation, crack growth, and catastrophic failure. a.) Under high stress, the crack growth phase can only be maintained for a relatively low number of cycles before failure. Consequently, this results in a much smaller crack growth zone compared to b.) low stress conditions [105].

In addition to applied stress, the crack size will have a significant impact on the stress intensity factor at the crack tip. It is well established that porous defects inherited from the fabrication process have a negative impact on fatigue properties [51], [78], [97], [106]. As we have discussed, these defects effectively act as cracks, and consequently lead to higher stress intensity factors, accelerating the process of fatigue damage. As the stress intensity factor is largely dependent on crack size, these effects are more apparent for large defects. Consequently, the maximum defect size is a more crucial indicator of fatigue performance compared to gross porosity [51], [97], [106]. Notably, variability in the maximum defect size between samples has contributed to instances of high fatigue scatter. Such effects have been accounted for by correlating the critical defect size with the resultant fatigue properties [106]. As LoF defects are typically much larger than gas entrapment or keyhole type defects, they typically can be associated with a more detrimental impact on the fatigue performance.

Despite the significance of these effects, a limitation of traditional LEFM is the assumption of an idyllically sharp pre-existing crack. However, practically the emergence of stress concentrations may arise around features that are less severe than an idyllic crack [104].

Taking these effects into account the radius of curvature of the crack tip (ρ) is often considered. As ρ tends to zero, the theoretical stress at the crack tip tends to infinity [51]. Consequently, this effect has a significant impact arising around the morphology of porous defects. Among the defect types inherited through SLM fabrication, LoF defects typically exhibit the largest degree of irregularity. As a result, LoF can be associated with a smaller effective radius of curvature, and consequently with higher stress concentrations and poorer fatigue properties [51].

Another limitation of LEFM is the assumption of a small plastic zone ahead of the crack tip [100]. However, this is not necessarily the case in titanium alloys for LCF loading regimes. Due to the high stress cycles inherent to LCF, deformation in the crack growth zone is predominantly characterised by plastic deformation [99], [101]. Consequently, resistance to LCF is derived from the effects of both crack nucleation and crack growth. Despite this, as the achievable fracture toughness of titanium alloys is relatively low, practically the fatigue life under such conditions is more extensively a consequence of the crack nucleation phase. Due to the lower stressing cycles inherent to HCF, a smaller plastic zone exists at the crack tip, and consequently, HCF is characterised by predominantly elastic deformation [99], [101]. As a result, resistance to HCF fatigue is predominantly derived from resistance to crack nucleation.

2.2.3.2 Surface Roughness

Surface roughness is also understood to have a detrimental effect on the mechanical properties of SLM fabricated components. In addition to defect size and shape, the proximity of defects to the free surface is often viewed as a critical factor in predicting the fatigue behaviour [97]. For porous defects on, or close to the surface, the stress and strain distribution is biased. This occurs because one side of the pore is exposed to a free surface, while the other side is exposed to the bulk of the material. The free surface provides less constraint to plastic flow than the bulk of the material, and consequently stress on the inside facing surface is intensified. As a result, defects on, or close to the free surface are typically associated with higher stress intensity factors, typically resulting in early crack initiation [107], [108]. This effect can also be observed for defects close to the free surface. However, as plastic flow is more constrained in the bulk of the material, a tapering off of these effects is generally observed alongside distance from the free surface (Fig 2.14). Consequently, the fatigue properties of SLM fabricated components is typically dictated by surface defects, rather than internal defects [23], [24], [101], [109], [110].

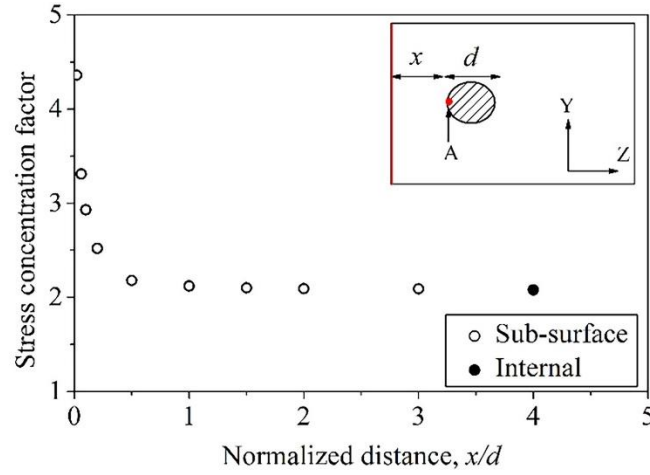


Figure 2.14. **Defect location.** Defects closer to the free surface are associated with higher stress concentrations [107], [108].

2.2.3.3 Morphology

As discussed in Section 2.2.2.3, surface defects result in a new class of irregularity in small diameter struts, which can be categorized as morphological. Broadly, morphological irregularities describe deviations between the as-designed and as-fabricated geometries [71], [72], [73], [74]. Such inaccuracies have had a significant impact on the prediction of the mechanical behaviour of lattice structures [20]. This largely stems from a misjudgment of the amount of material that is load bearing. In lattice structures, this extends to strut oversizing or undersizing. Oversizing beyond the as-designed geometry may lead to an increase in stiffness and strength, while undersizing may lead to a reduction. These effects are noticeable by only small changes in strut diameter [111].

2.2.4 Biological properties

As discussed in Section 2.2.2.2, the surface of SLM fabricated components is inherently rough. Applied to biomedical implants, surface roughness and topology play an important role in regulating cell behaviour [21]. Cells which come into contact with the surface, recognise roughness and topological features as biophysical stimuli. Subsequently, these stimuli are converted into a cellular response via the process of mechanotransduction. Complex signalling pathways are activated through the relay of stimuli through integrin activity, stretch activated ion channels, or cell-surface receptor proteins. This ultimately results in the regulation of gene transcription, which consequently controls cellular functions and phenotypes [21], [112], [113], [114].

Considering these effects, the surface topology of SLM fabricated lattice structures is crucial to the modulation of cell behaviours in biomedical implants. Among topological features, surface roughness plays a crucial role in mediating cell behaviour [21], [25]. It is

becoming increasingly apparent that both overly smooth and overly rough surfaces are not conducive to either cell attachment or osteogenic differentiation. Excessively smooth surfaces may lack sufficient topological features to activate mechanotransduction through shear induced modulation of the actin cytoskeleton [21], [25], [115]. On the contrary, excessively rough surfaces may also be not ideal. Here, cells may adapt their morphology to minimise contact with high energy topological discontinuities, which consequently hinders f-actin formation or cell spreading, and in turn limits mechanotransductive signalling. [21], [25]. These effects have been demonstrated conclusively on a range of materials [21], [25].

2.2.5 SLM fabrication of titanium and titanium based alloys

2.2.5.1 Crystallographic structure

Titanium is an allotropic material with more than one crystallographic form. At lower temperatures, pure titanium adopts a hexagonal close-packed (hcp) structure, and is referred to as the α -phase (Fig 2.15.a) [116]. In the α -phase, the c/a ratio represents the relationship between height (c) and the basal plane side length (a). With a c/a ratio of 1.587, the HCP structure of pure titanium represents a relatively flattened configuration compared to the ideal HCP value of 1.633 [116]. As discussed in Section 2.2.5.3, the anisotropy of this configuration has a significant effect on mechanical properties.

Above the β -transus temperature (882.5°C), pure titanium adopts a body-centered cubic structure, and referred to as the β -phase (Fig 2.15.b) [116]. The crystal structure of β -phase has more symmetry than the α -phase, and is consequently described by a single lattice parameter (a); which in pure titanium is measured as 0.332nm. Due to this symmetry, the β -phase has a higher configuration entropy, and is consequently favoured at higher temperatures.

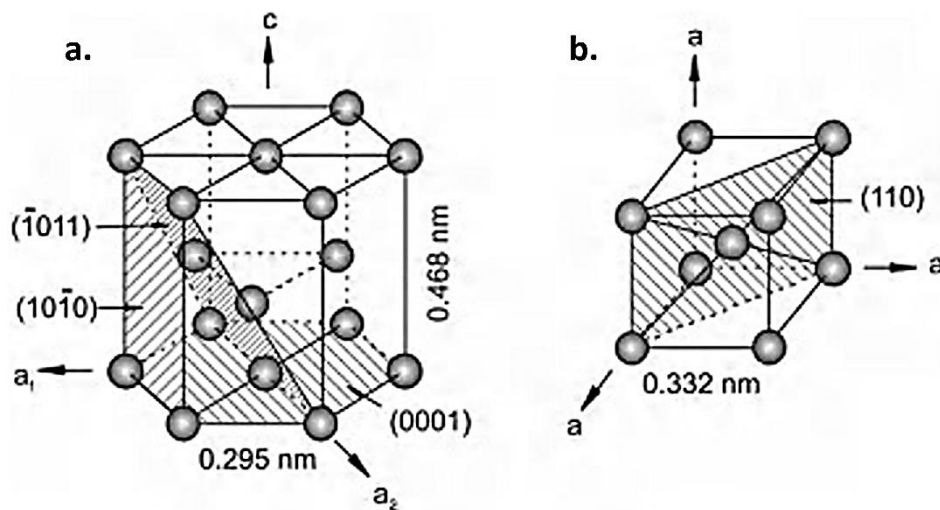


Figure 2.15. **Crystallographic Structure of titanium and titanium alloys.** a.) The HCP structure of the α -phase, with lattice parameters representative of pure titanium. b.) The BCC structure of the β -phase, with lattice parameters representative of pure titanium [116].

2.2.5.2 Phase composition

The β -transus temperature is the limiting temperature between the α -phase and the β -phase. In pure titanium, it is measured as 882.5°C, but may be adjusted through the addition of alloying elements or impurities (Fig 2.16.d) [116], [117].

Alloying elements are broadly categorised depending on whether they increase or decrease the β -transus temperature [116], [118]. α -stabilizing elements increase the β -transus temperature by stabilizing the α -phase (Fig 2.16.a). β -stabilizing elements can be further categorised into β -isomorphous formers and β -eutectoid formers. β -isomorphous formers are completely soluble within the β -phase, and enhance stability (Fig 2.16.b). On the other hand, β -eutectoid formers are comparatively less soluble in the β -phase, consequently introducing intermetallic compounds (Fig 2.16.c).

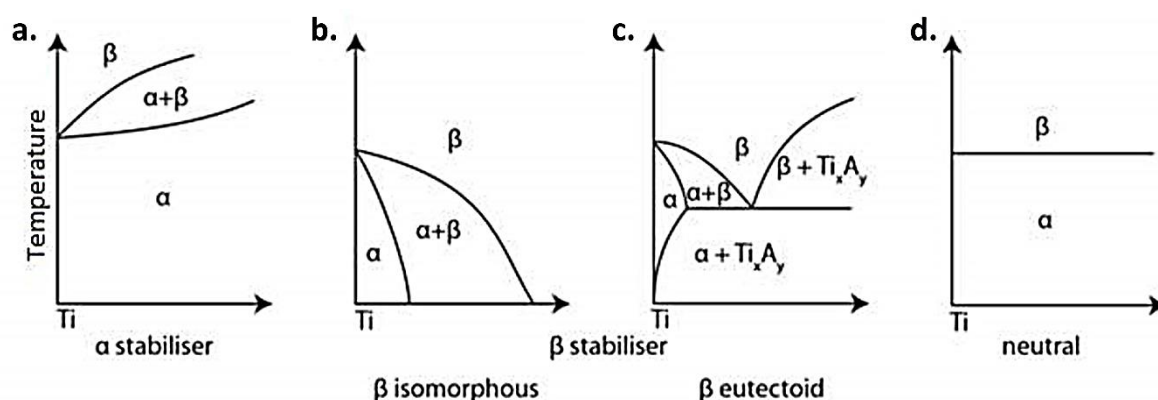


Figure 2.16. **Phase Composition of titanium alloys.** The effect of alloying titanium can be categorised as a.) α stabilizing, b.) β -isomorphous, and c.) β -eutectoid. This is in comparison to a purely temperature dependent α/β transformation in pure titanium [116].

With the above in mind, Ti-6Al-4V is considered an α - β titanium alloy. Aluminium alloying along with trace amounts of oxygen contributes to the stability of the α -phase, while vanadium contributes to the stability of the β -phase [116], [118]. Together, these alloying elements allow Ti-6Al-4V to combine the strength of the α -phase with the ductility of the β -phase, while also remaining adaptive, by remaining susceptible to heat treatment. β -eutectoid formers have little relevance to Ti-6Al-4V, as the focus is on maintaining a dual-phase structure rather than eutectoid transformations.

Due to this susceptibility to heat treatment, the final phase composition of Ti-6AL-4V is strongly influenced by thermophysical processing. These effects can be estimated using

continuous cooling transformation (CCT) curves, which describe the relationship between cooling rates and phase composition (Fig 2.17) [119]. Under slow cooling below the β -transus temperature, the transformation from β to α occurs through diffusion based nucleation and growth. As further discussed in Section 2.2.5.3, this gives rise to a laminar microstructure, characterized by a series of plate-like α precipitates (α laths), separated by thin layers of retained β . In addition to the primary α and β phases, martensite α' and orthorhombic martensite α'' phases are also possible. During rapid cooling, the $\beta \rightarrow \alpha$ diffusional process can no longer be accommodated, in which case a diffusionless transformation into the hcp metastable α' martensite phase takes place, involving the cooperative movement of atoms through a shearing mechanism [118].

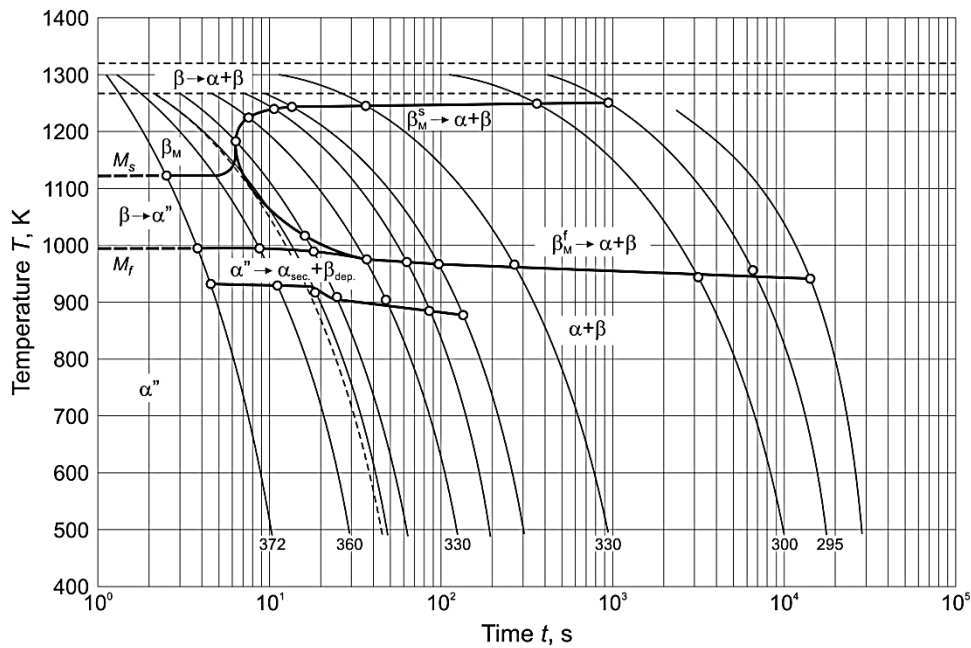


Figure 2.17. **Continuous cooling transformation curve for Ti-6Al-4V.** The CCT curve describes the relationship between cooling rates and phase composition [119].

Due to the rapid cooling rates inherent to SLM processing, the final as-built microstructure is more often characterised by this α' martensite phase [15], [118]. However, the prediction of the final phase composition is further complicated due to cyclical reheating by parallel laser passes, and by processing of subsequent layers (Fig 2.18) [120]. If the reheating temperature exceeds the β -transus temperature, recrystallisation into the β -phase can occur, which due to lower thermal gradients during subsequent cooling may result in an $\alpha + \beta$ composition. This is effectively an annealing process, however, due to very short hold times above the β -transus, only a small amount of α' is absorbed into the β -phase, consequently resulting in a $\alpha' + \alpha + \beta$ composition. Despite this possibility, the thermal

profile during SLM processing is highly localized, and entirely α' martensite compositions are most commonly observed [15], [121].

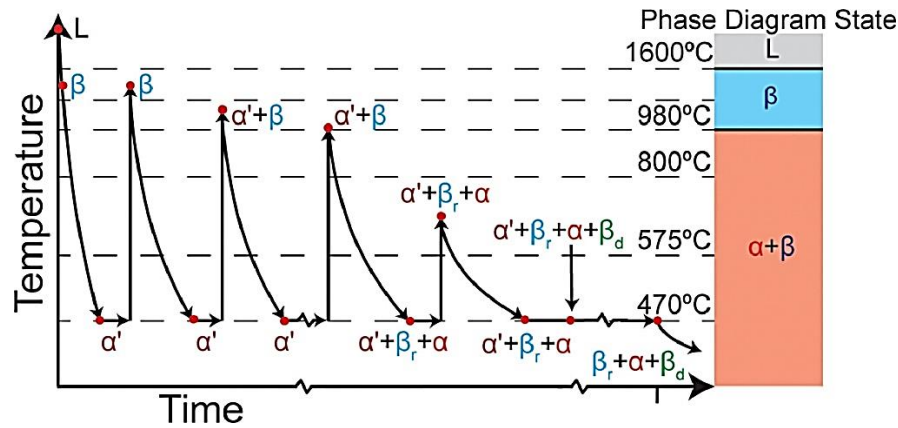


Figure 2.18. Cyclical reheating during SLM processing. Possible phase transformations of Ti-6Al-4V during SLM processing due to cyclical reheating by parallel laser passes, and by processing of subsequent layers [120].

2.2.5.3 Microstructure

As an α - β alloy, a broad range of microstructures are possible in Ti-6Al-4V. However, before heat treatment, or work hardening, the final microstructure is typically lamellar [15]. As briefly discussed in Section 2.2.5.2, this microstructure is derived from the nucleation and growth of α -laths within the prior- β grains. During this transformation, α/α' generally grows with a Burger's orientation relationship (OR) with the β -phase described by parallel planes $\{0001\}_\alpha || \{110\}_\beta$ and parallel directions $\langle 11\bar{2}0 \rangle_\alpha || \langle 1\bar{1}1 \rangle_\beta$, providing an interface with the lowest total dislocation energy [120], [122], [123]. Since there are six equivalent $\{110\}$ close packet planes, and two equivalent $\langle 1\bar{1}1 \rangle$ close packet directions on each plane in the β -phase, twelve variants of α/α' phase are possible, with five unique relationships when symmetric equivalence is considered (Fig 2.19) [120], [122], [123].

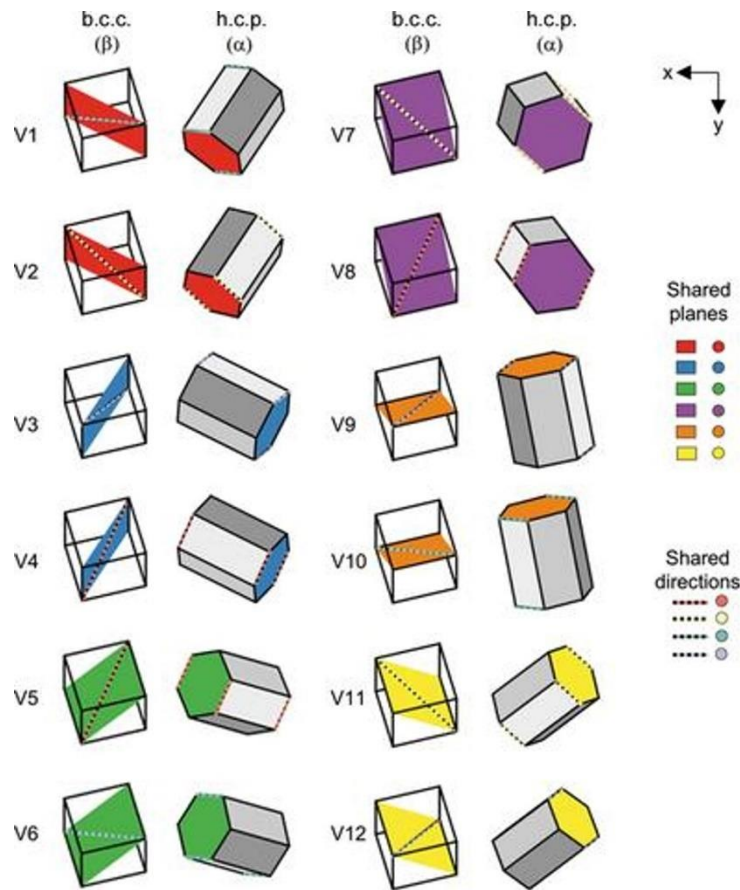


Figure 2.19. **Burger's orientation relationship during BCC to HCP transformation.** The Burgers orientation relationship defined by parallel planes $\{0001\}_\alpha || \{110\}_\beta$ and parallel directions $\langle 11\bar{2}0 \rangle_\alpha || \langle 1\bar{1}\bar{1} \rangle_\beta$, allows for twelve possible variants of the HCP phase [123].

As the α -phase nucleates at the prior- β grain boundaries, they grow into the β grain as colonies of parallel laths, sharing the same variant of the Burger's OR. These colonies grow into the β grain until they impinge on each other, resulting in a characteristic lamellar structure (Fig 2.20) [124]. As cooling rates are increased, nucleation is favoured over propagation and colonies begin to nucleate on the boundaries of other colonies, resulting in a higher number of variants and a smaller colony and lath size [15]. With faster cooling rates, this typically yields an interweaved microstructure. This process, as well as the Burger's OR is also followed during the $\beta - \alpha'$ transformation [123]. However, due to rapid cooling, this occurs through the movement of atoms through a shearing mechanism, rather than diffusion.

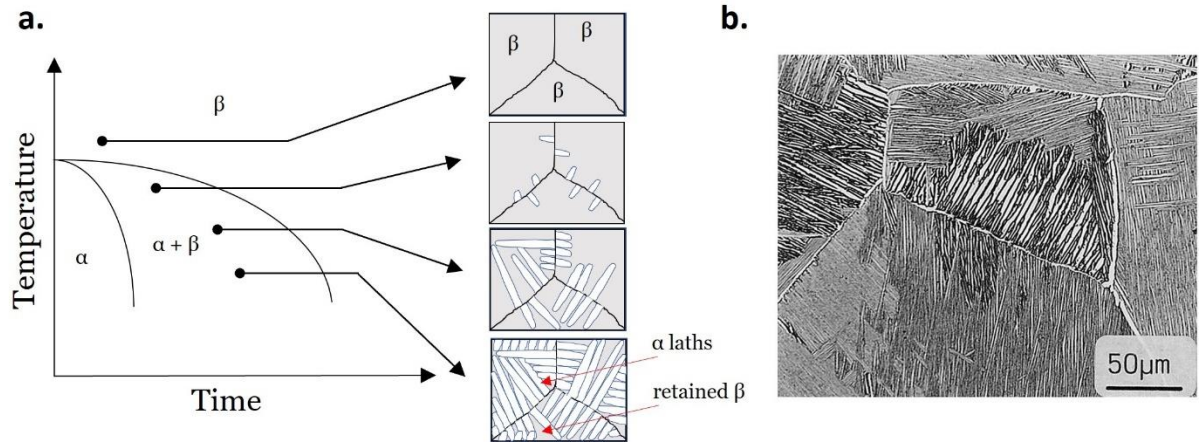


Figure 2.20. **β to $\alpha + \beta$ phase transformation.** a.) As the temperature drops below the β -transus, the α -phase nucleates at the prior- β grain boundaries, and grow into the β grain as colonies of parallel laths. b.) This results in a typical laminar microstructure of α laths separated by the retained β phase [124].

During SLM fabrication, the titanium powder is heated well above its liquidus temperature. As the heat source moves away from this point, the thin layer of liquified material rapidly solidifies into the β -phase. Due to the layer wise nature of SLM, strong thermal gradients develop parallel to the build direction, and drive directional solidification. As subsequent layers are processed, the top of these grains are remelted, and act as a nucleus for epitaxial growth; consequently leading to the development of a coherent columnar grain structure [125], [126].

Following solidification, the high cooling rates inherent to SLM typically drive a $\beta - \alpha'$ transformation. However, as discussed in Section 2.2.5.2, the evolution of the final microstructure is further complicated by cyclical reheating [120]. As discussed, reheating above the β -transus temperature, combined with a slower cooling rate may yield a more complicated $\alpha' + \alpha + \beta$ [120]. Despite this, the majority of studies have reported entirely α' microstructures as a result of SLM processing [15], [121]. This could be expected even if reheating occurs above the β -transus, if the subsequent cooling cycles are above the critical cooling rate for α' transformation (410°C/s). This process has been demonstrated to yield a hierarchical structure of α' , typical of SLM (Fig 2.21) [121]. On the first cycle of cooling, primary α' laths precipitate from the prior- β grain boundaries. Generally, these typically extend across the entire parent β grain, or until they impinge on another α' variant. Reheating above either the β -transus or martensite start temperature (M_s), followed by rapid cooling, may yield the precipitation of finer secondary laths which nucleate on the broad face of the residual primary laths, and consequently grow roughly perpendicularly. This has also shown to extend into tertiary and quartic laths [121], [127]. Due to the large number of variants that precipitate during this process, the α' phase generally exhibits an inherently weak texture in SLM [123].

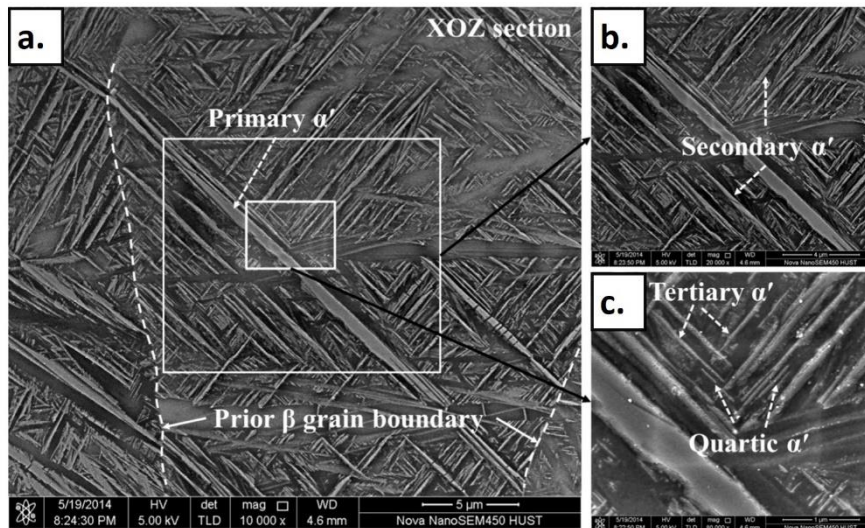


Figure 2.21. **Typical hierarchical α' microstructure from SLM manufacturing.** The SLM fabrication process typically results in a hierarchical α' microstructure within the prior- β grains, and generally characterised by a.) primary, b.) secondary, and often c.), d.) tertiary and quartic laths [121].

2.2.5.4 Mechanical properties

Under loading, deformation occurs in a material which up to the yield point is characterised by an elastic behaviour [79]. These properties are largely influenced by the anisotropy of the lattice structure. In HCP materials, the close packed plane $\{0001\}$ and close packed direction $\langle 1120 \rangle$ represent a higher density of atomic packing, and consequently loading along the c-axis is associated with higher stiffness. Generally, this leads to an increase in stiffness for grains with their c-axes aligned close to the global loading direction (Fig 2.22) [128], [129].

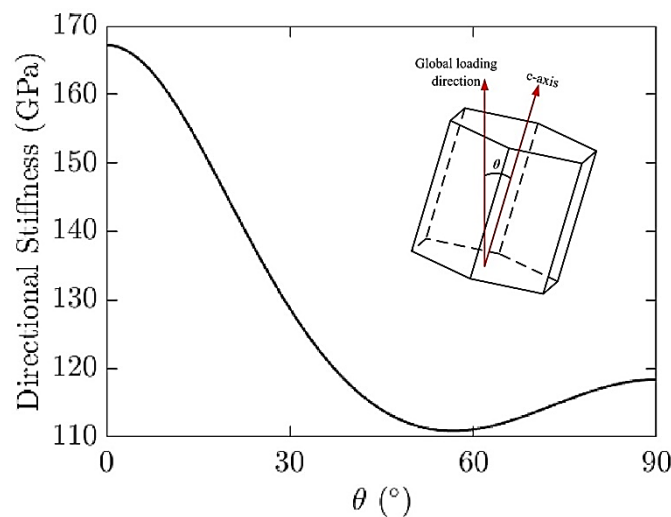


Figure 2.22. **Elastic anisotropy of HCP Ti-6Al-4V.** The c-axis is often associated with higher stiffness due to the strong atomic bonding along this direction [129].

If loading continues beyond the yield point, the material will continue to deform plastically [79]. This occurs through the rearrangement of atoms, accommodated by dislocations or twinning. However, twinning is considerably suppressed in Ti-6Al-4V as a consequence of the high aluminium content [128], [129]. Consequently, dislocation slip is commonly considered as the primary mechanism of deformation [128], [129], [130]. Characterised as a crystallographic discontinuity, dislocations move through the grain, allowing the material to plastically deform without completely destroying the crystal structure. Consequently, this process characterises the onset of yielding. Due to the low symmetry of the HCP lattice, the number of slip planes is limited compared to the BCC lattice. In HCP materials, slip is accommodated on basal, prismatic and pyramidal planes [128], [129] (Fig 2.23). The relative strength of each slip plane contributes to plastic anisotropy.

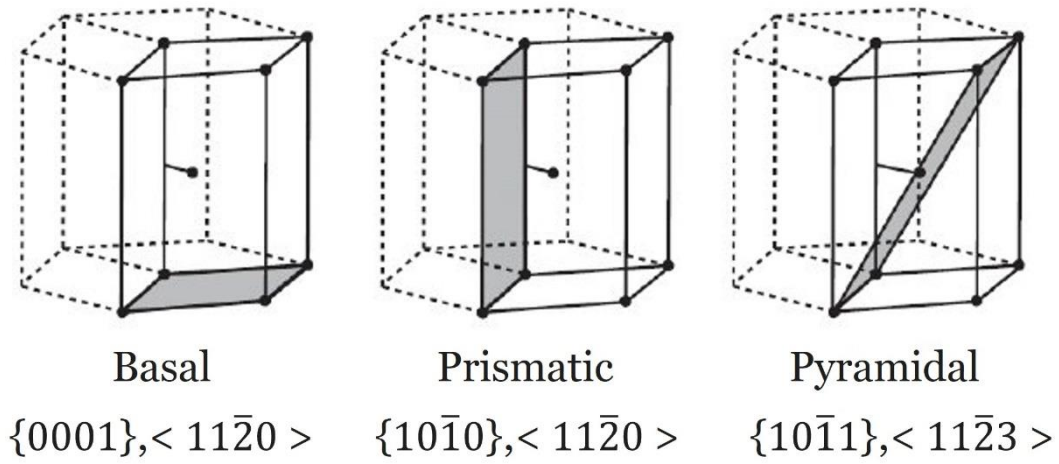


Figure 2.23. **HCP slip systems.** Possible slip systems in the HCP lattice include Basal (left), Prismatic (middle) and pyramidal (right) [131].

The $\langle a \rangle$ basal and $\langle a \rangle$ prismatic slip systems are more easily activated than $\langle c + a \rangle$ pyramidal slip [129]. Generally, the basal slip plane is also considered slightly weaker than the prismatic slip plane, however a number of studies have also suggested the contrary [129]. Despite this, activation of a particular slip system is not only determined by its relative strength but also by the critical resolved shear stress (CRSS) acting on the slip plane. The CRSS describes the stress acting on a particular slip system due to the applied load, and is consequently largely determined by the orientation of the lattice to the applied load [132]. This relationship can be described by the Schmid factor [133]. With Fig 2.24 in mind, the resolved shear stress can be calculated using Schmid's law as follows.

$$\text{resolved shear stress} = \frac{\text{resolved force}}{\text{slip plane area}} = \frac{F \cos \lambda}{A / \cos \phi} = \frac{F}{A} \cos \lambda \cos \phi \quad \text{Eq. 5}$$

Consequently, the Schmid factor ($\cos \lambda \cos \phi$) relates the applied force to the resolved shear stress acting on a particular slip system [132]. If the resolved shear stress exceeds the critical resolved shear stress, dislocation slip will be activated on that plane. Ranging from 0 to 0.5, the Schmid factor ($\cos \lambda \cos \phi$) reaches a maximum at $\phi = 45^\circ$; indicating a favourable lattice orientation to the applied load for activation of a slip system.

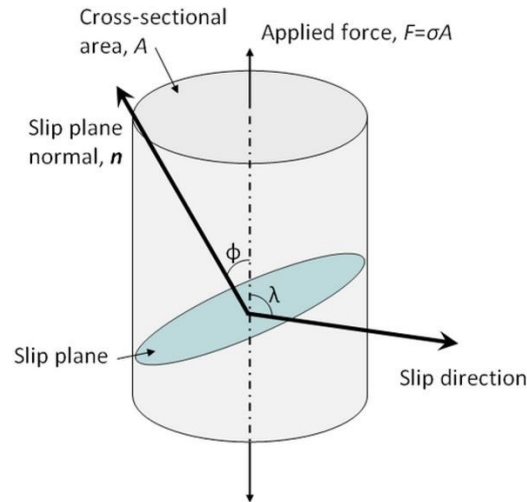


Figure 2.24. **Schmid's Law.** The Schmid factor governs how externally applied stress is translated into resolved shear stress on each slip plane [132].

On activation of a slip system, the movement of dislocations continues until they reach a grain boundary, where they are blocked due to the barrier generated by the lattice orientation mismatch [134]. As loading continues, more dislocations pile up against the grain boundary. Due to the repulsive force between dislocations, this results in a concentration of stress, ultimately driving the propagation of dislocations across the high energy grain boundary. Consequently, pile-up reduces the necessary applied stress for the continuation of plasticity. In smaller grains, the possible number of dislocations piling up decreases, and consequently, a higher applied stress is required for the propagation of dislocations across the grain boundary [134]. As described by the Hall-Petch relationship, this effect drives an inverse correlation between grain size and strength. However, alongside these effects, a reduction in grain size is also associated with a reduction in the strain to failure in Ti-6Al-4V. This is associated with a reduced possible dislocation slip length, consequently impeding plastic flow [134].

Grain boundary effects continue to strengthen the material up to the ultimate tensile/compressive strength. Beyond this point, ductile materials tend to exhibit failure characterized by micro-void growth and subsequent coalescence. This gives rise to a drop in engineering stress and eventually to total failure. As discussed in Section 2.2.2.1, some level of porosity is almost always present in SLM fabricated material, in the form of micro-

voids, and acts to accelerate failure mechanisms. However, in the absence of existing pores or inclusions, void nucleation is also enabled by local plastic deformation at material heterogeneities [135], [136]. In the absence of inclusions, clustering of atomic vacancies (vacancy condensation) appears to be the primary mechanism of void nucleation in metals that deform by slip [135], [136]. Following this, growth occurs by absorbing dislocation loops, and consequently is accelerated in areas of elevated dislocation density [135]. Contrarily, inclusions are a common occurrence in SLM fabricated Ti-6Al-4V, and can also act as a crux for void nucleation [136], [137]. It is generally accepted that this occurs through either inclusion cracking, or decohesion.

2.3 Conclusion

Additive manufacturing techniques such as PBF have enabled biomedical implants to be fabricated with a high level of design freedom [10], [11]. As a result, implants can be tailored to patient specific anatomies, ensuring a precise fit and an enhanced level of surgical success [14]. Combined with the macro geometry of a patient specific implant, a geometrically complex lattice structure can be adopted as an infilling pattern, allowing the implant to be fabricated as a porous structure. Compared to traditional non-porous implants, these lattices have shown great potential for bone repair [8], [9]. The lattice architecture can be designed to achieve a tailored mechanical or biological response, such as to recapitulate the stiffness gradients of the native tissue or to allow bone ingrowth [8], [9], [44], [46], [47]. The high resolution of PBF has lent itself well to such applications, where subtle changes in the lattice architecture (in the order of a few tens of microns) can have a significant impact on its properties, and the surgical success of the implant [8], [9].

Despite the near net shape capabilities of PBF, defects are commonly inherited from the fabrication process, which limit the potential to fabricate porous implants with a predicted, or for a fine-tuned response [15], [16]. The inheritance of these defects extends to internal porosity, a fine-grained α' martensite microstructure, and topological defects such as partially adhered powder [17], [18]. For non-latticed structures, such as traditional non-porous implants, the inheritance of these defects has been comprehensively linked to a degradation of mechanical properties, and as a result, a large number of studies have focused on minimising their effects [51], [138]. This has been largely achieved through the refinement of in-process printing parameters, or by the adoption of post-processing techniques [17]. For example, internal porosity can be minimised by refinement of the in-process laser parameters, while surface roughness can be minimised using post-process surface cleaning techniques such as polishing or grinding [115], [139].

On account of a small feature size, these defects are often inherited disproportionality in lattice structures [19], [20]. This can result in a degradation of mechanical properties compared to traditional bulk-sized components [19]. However, these effects have been typically studied in full lattice structures, and as a result, have been complicated by geometrical variations between different lattice designs. Further research is needed to characterise the bulk mechanical properties of the material as a function of basic architectural features of the lattice, such as strut diameter. This is critical from a design perspective, as the characterisation of such properties is fundamental to the prediction of mechanical performance and failure mechanisms.

By extension of this topic, the minimisation of process inherited defects through parameter optimisation is an important aspect of additive manufacturing [17]. This procedure is largely dependent on an understanding of the inheritance of these defects. For example, porous lack of fusion defects may arise due to insufficient melting of the powder material. As a result, parameter optimisation can be achieved by increasing the laser energy density input [51]. As we have discussed, these defects are inherited disproportionately in lattice structures. Although these effects are well-documented in full lattice structures, their inheritance is poorly understood as a function of fundamental architectural features of the lattice, such as strut diameter. As a result, our ability to adapt processing parameters to mitigate these effects has been limited.

However, not all defects can be minimised through the optimisation of process parameters [140]. Topological defects such as partially adhered powder are largely unavoidable [64]. On account of the small feature size lattice architecture, these defects represent a high portion of the total volume of the lattice, and as discussed, are detrimental to mechanical properties. Although these defects can be minimised using post-process surface cleaning, the majority of these techniques rely on a line of sight with the material, and are ill-suited to the internal features of the lattice.

In regard to the biological response of the implant, the inheritance of defects has another significant role to play. Through the effects of mechanotransduction, the response of cells coming into contact with the implant is strongly influenced by the surface topology [21]. In this regard, a number of recent studies have investigated the potential of leveraging the aforementioned surface cleaning techniques to improve the osteoinductive qualities of the implant [22]. However, the outcome of this work has been varied. On the one hand, the as-built surface has been shown to be excessively rough for osteogenic differentiation, and better results have been observed after post-process surface cleaning [21], [25]. On the other hand, surface cleaning can also lead to unfavourably smooth surfaces, with superior results observed on the rough as-built surface before any post processing [21], [25], [115].

In other materials, mechanotransductive effects have been studied across a gradient of topologies, and it is becoming apparent that both overly rough and overly smooth surfaces are not conducive to osteogenesis, and likely a middle ground exists [21], [25]. For additively manufactured surfaces, it is difficult replicate these studies. Different surface topologies have been created using a combination of surface cleaning techniques. However, with this approach, the as-built features are either removed or they are not, not as a gradient.

Chapter 3: Feature size specific processing parameters for Ti-6Al-4V micro-strut lattices fabricated by powder bed fusion

This chapter is under review in the Journal of 'Mechanical Behaviour of Biomedical Materials', under the title 'Feature size specific processing parameters for additively manufactures Ti-6Al-4V micro-strut lattices', and co-authored by Conor O'Keeffe, Wenyong Zhang, Robert D Johnston, Patcharapit Promoppatum, David Taylor, Caitríona Lally, and Daniel J Kelly.

P, P wrote the material UMAT subroutine utilised in computational modelling. W, Z and R.D, J provided expert opinions on the computational modelling approach. D, T provided expert opinion on fracture mechanisms. C, L and D.J, K supervised this work.

Abstract

The material properties of individual micro-struts are critical to the overall success of lattice structures. These properties can be significantly compromised by defects inherited from powder bed fusion processes. Among these defects, porous inclusions are well understood to have a detrimental effect on mechanical properties; posing a high risk to the implant under loading. While the majority of these defects can be avoided through optimisation of printing parameters, this has generally only been done for traditional bulk components with no in-designed porosity. However, a number of studies have observed changes in the frequency of such porous inclusions as feature size is reduced, indicating a size effect. This also suggests that the optimal parameters for bulk material are not necessarily translatable to the individual micro-struts which build the lattice.

In this study, the relationship between parameter optimisation and feature size was investigated. Here, a higher energy density input was required for processing micro-strut lattices with an optimised relative density, than it was for bulk components. This could be attributed to faster rates of heat loss in micro-strut samples on account of their increased surface-to-volume ratio. The consequential improvement in mechanical properties was also assessed. An increase in both strength and stiffness could be largely attributed to an increase in the percentage volume of load bearing material, while improvements in failure strain were largely driven by the minimisation of stress concentrations around the irregular pore morphologies. Fatigue properties did not improve beyond the effects of yielding. Rather, crack initiation was dominated by surface defects; which on account of their surface free energy, experienced a much higher stress intensity factor.

3.1 Introduction

Selective laser melting (SLM) additive manufacturing techniques have enabled the development of porous metallic lattice structures with unique properties, otherwise unachievable by the parent material [44], [46]. When applied to biomedical applications such as orthopaedic implants, such lattices offer many advantages over traditional non-porous implants, such as supporting bone ingrowth and tailorable mechanical properties [8], [9], [44], [45]. The mechanical properties of these lattice structures are critical to their overall success as orthopaedic implants, as they not only determine structural stability under loading, but also bone growth and osteointegration, as such processes are regulated by the local mechanical environment. Through the control of various design parameters such as unit-cell topology, or strut size, mechanical properties can be tuned to closely recapitulate cortical (3-30GPa) and trabecular (0.05-2GPa) bone [8], [9], [44], [46], [47]. However, not all these designs will be supportive of bone growth and osteointegration, which also requires cell migration and sufficient nutrient exchange [45]. In general, lattice porosity in the range of 50-90% is considered optimal for osteointegration [8], [45], [48]. Consequently, only a narrow range of lattice designs meet all considerations for use as bony implants or scaffolds for bone regeneration, generally demanding a delicate balance between ensuring sufficient implant strength and stiffness, but a low volume fill fraction to impart porosity [8], [44], [45], [48]. This highlights the importance of both implant geometric design and material selection for such orthopaedic applications.

Due to its mechanical properties, corrosion resistance and biocompatibility, Ti-6Al-4V has a long history of use in orthopaedic implants and bone tissue engineering applications [9]. However, the integrity of this material can be significantly compromised due to defects inherited from the PBF fabrication process [81], [141], [142], [143], [144]. Fortunately, the majority of these defects can be minimised through optimisation of printing parameters [142], [144]. One of the most important aspects of such optimization is the control of internal porosity, a known driver of reduced strength and failure strain [81], [143]. These defects can be minimised through optimisation of the energy density input [142], [144]. This must be high enough to sufficiently melt the material, but also low enough to avoid gas entrapment or keyholing. Consequently, parameter optimisation is fundamental to PBF fabrication. For bulk materials, the window of suitable printing parameters is well characterised [142], [144], however less attention has been paid to optimising manufacturing parameters for lattice structures.

Despite this, the application of lattice structures continues to increase. Many studies have reported on the engineering mechanical properties of different designs. However, only a few have attempted to characterize the bulk mechanical properties of the micro-strut building blocks [72], [141], [145], [146]. These studies have sought to decouple the

influence of the geometry of different lattice designs by using micro-strut dog-bone geometries, printed on the same scale as the micro-strut building blocks that make up the lattice. From this work, it is becoming apparent that the mechanical properties of such micro-struts can be significantly different to the bulk material. It is also clear that these effects are largely driven by the disproportionate uptake of process inherited defects in small diameter struts [71], [141], [145]. This extends to the aforementioned effects of internal porosity [146], [147], [148]. These studies have shown a discrepancy in the frequency of such porous inclusions as feature size is reduced, indicating a size effect, and that the optimal processing parameters for bulk (i.e., non-porous) materials are not necessarily translatable to the individual micro-struts which build a lattice. Therefore, the objective of this study is to investigate the relationship between processing parameters and feature size for Ti-6Al-4V, and in doing so, to maximise the mechanical properties of micro-struts through the adoption of feature size specific printing parameters.

3.2 Methods

3.2.1 Design & manufacturing

Samples were designed using the computer-aided-design (CAD) software Autodesk Netfab and Autodesk Inventor (Autodesk, San Francisco, Ca). Micro-strut samples were designed as cylindrical dog-bones geometries of various gauge diameters ($\varnothing 500$ and $700\mu\text{m}$). Dimensional ratios proportional to ASTM E8 were maintained [149]. Lattice samples were designed as a 5mm^3 structure, homogenously infilled with a 2mm^3 body centred cubic (BCC) unit cell and $\varnothing 500\mu\text{m}$ strut size. Bulk samples were designed as a 5mm^3 cube with no in designed porosity.

All samples were fabricated from Ti6Al4V, Grade 23 (particle size = $10\text{-}45\mu\text{m}$) powder. The powder material was processed on a Realiser SLM 50 manufacturing system (DMG MORI, Bielefeld, Germany) using a pulsed laser (emission wavelength = 1070nm) calibrated to a spot size of $160\mu\text{m}$. An argon-controlled atmosphere ($\text{o}_2 < 0.2\%$) was maintained throughout the process. For each design, the CAD geometry was processed in slices of $0.25\mu\text{m}$. Each slice was scanned by the laser using a contour-and-hatch (C&H) scanning strategy. Parameter optimisation was achieved by varying laser exposure time on the inner hatching scan tracks in increments of $33\mu\text{s}$ from 0 to $264\mu\text{s}$. As detailed in Table. 3.01, all other parameters were kept constant.

After printing, electrical discharge machining (EDM) was used to remove samples from the build plate. Following this, they were sonicated in isopropyl alcohol for 30 minutes to remove loose powder.

Table 3.01. Metal constructs were processed with a contour-and-hatch laser scanning strategy. In this approach each slice of the CAD geometry is processed by the laser with an outer scan, which traces the contour boundary of the CAD geometry (Contour Scan). Subsequently, the enclosed area is filled with inner scans which trace a hatching pattern (Hatch Scan).

Hatch And Contour Scans		Hatch Scan		Contour Scan	
Layer Thickness	25µm	Exposure Time	33-264µs	Exposure Time	33µs
Spot Size	160µm	Power	100W	Power	100W
Point Distance	10µm	Hatch Spacing	100µm	Offset from CAD boundary	100µm
Point Distance	10µs	-	-	-	-

3.2.3 Porosity analysis

Parameter optimisation was conducted by varying laser exposure time in 1.) the micro-strut samples, representing the basic building blocks of lattice structures, and 2.) the bulk samples, representing traditional non-porous AM. Porosity was characterised in each sample by 2D image analysis of metallographic cross-sections; taken longitudinally to the sample and parallel to the printing direction. For this analysis, the micro-strut samples were simplified to thin cylindrical struts, with the same height and guage diameter as the dog-bone designs. This was required for localisation of the ø500 and 700µm cross-sections, as-well as providing a larger total surface for porosity calculations.

The preparation of these cross-sections entailed a sequential grinding/polishing metallographic protocol. Samples were mounted along their longitudinal axis in conductive SEM resin using a TA automated mounting press, and passed through a sequential grinding and polishing protocol (Grinding: P800, P600, P1500, P72500 for 1min/step at 30MPa, 150rpm, complimentary rotation, and water lubricated. Polishing: 0.3µm Fume Silica (Labquip, Ireland), for 10min at 20MPa, 150rpm, complementary rotation), and finally sonicated in an alcohol solution for 30 minutes.

Samples were imaged at x5 magnification using a Zeiss ULTRA inverted microscope (Carl-Zeiss-Stiftung, Heidenheim, Germany). Stitching was required to cover the entire sample area. Images were then re-segmented into manageable chunks (2048 x 2048 pixels) and passed to ImageJ's machine learning plugin *trainable weaka segmentation* for

identification of porous, metallic and background pixels. Porosity and pore size were then calculated using the *analyse particles* plugin.

3.2.4 Thermal modelling

The thermal histories along the C&H scan tracks were estimated using a gaussian distributed surface heat flux model in the finite element (FE) solver Abaqus Explicit (Dassault Systèmes Simulia corporations, Vélizy-Villacoublay, France). However, due to the computational intensity of this approach, it could not be extended to the entire build. Instead, a simplified heat input was used to capture the thermal accumulation of multi-layer deposition, and the Gaussian heat flux model was only considered on a final layer [150].

For the implementation of this approach, the computational domain was partitioned into an upper and lower region, mimicking the multiple layers of fabrication. In both cases, the domain was extended by an additional 0.5mm beyond the strut diameter, accounting for the build-up of unprocessed powder. The thermal histories across this domain were obtained by solving the transient heat conduction equation (Eq. 6). The upper region represented a final 0.25mm layer of powder, and was imposed by a Gaussian surface heat flux (Eq. 7) tracing the complex C&H scan tracks using a DFLUX subroutine [150], [151]. The lower region represented the multiple layers of deposition throughout the build, and was consequently partitioned into a solidified core and outer powder sleeve. The thermal accumulation in the solidified core was accounted for using a pre-defined temperature field. Heat losses from convection and radiation were considered on the top and side surfaces (Eq. 8).

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + q''(x, z) \quad \text{Eq. 6}$$

Where; ρ is density (kg/m^3), C_p is heat capacity ($J/kg/K$), and k is thermal conductivity ($W/m/K$).

$$q''(x, z) = \frac{2AP}{\pi r_0^2} \exp \left(\frac{-2((x-x_0)^2 + (z-vt)^2)}{r_0^2} \right) \quad \text{Eq. 7}$$

Where; A is absorptivity, P is power (W), r_0 is laser radius (m), and v is the scanning velocity (m/s).

$$q''_{loss} = h(T - T_{sur}) + \varepsilon \sigma (T^4 - T_{sur}^4) \quad \text{Eq. 8}$$

Where; h is the heat transfer coefficient ($W/m^2/K$), ε is emissivity, σ is the Stefan-Boltzmann constant ($W/m^2/T^4$), and T_{sur} is the surrounding temperature (K).

The computational domain was meshed using cubic heat transfer elements (DC3D8), and refined locally in the laser scanning area with a converged element volume of $1e^{-3} \mu m^3$

(and surface area <5 times smaller than laser spot size). A coarser mesh is used for the surrounding loose powder and solidified substrate.

The temperature and phase dependency of the Ti-6Al-4V material properties was considered for both the powder, and solidified core (Table. 3.02 and Table. 3.03). For the solidified core, the material state change was captured by a simple temperature dependent solid-liquid-solid transition. However, for powder, the material state change is more complicated. During SLM processing, the powder material undergoes an irreversible and temperature dependent powder-liquid-solid transition. This behaviour was captured in the model using a UMAT subroutine [150].

Table 3.02. The temperature and phase dependency of the Ti-6Al-4V material was considered for FE modelling [150].

T (°C)	30	230	430	630	830	1030	1230	1430	1653	1930
Solid to liquid										
k (W/m/K)	7	9	11	15	20	20	23	25	34	34
ρ (kg/m³)	4410	4390	4364	4332	4305	4270	4240	4200	3910	3737
c_p (J/kg/K)	540	600	630	680	720	650	680	720	830	830
Powder										
k (W/m/K)	0.57	0.57	0.57	0.58	0.63	0.74	0.78	0.80	0.80	-
ρ (kg/m³)	2652	2634	2618	2599	2583	2562	2544	2520	2520	-
c_p (J/kg/K)	540	600	630	680	720	650	680	720	830	830

Table 1.03. Temperature and phase independent FE modelling parameters [150].

Heat source absorption coefficient	A	0.3
Heat Transfer Coefficient ($W/m^2/K$)	h	11.4
Emissivity	ε	0.7
Stefan-Boltzmann constant ($W/m^2/T^4$)	σ	5.6704

3.2.5 Mechanical testing

Tensile tests were carried out on micro-strut samples under displacement control at a strain rate of 0.5%/s until failure. This was performed on a Zwick universal testing machine (Zwick Zoo5, Zwick GmbH & Co. Ulm, Germany) equipped with a 200N load cell. Using Matlab (MathWorks, Cambridge, UK), the cross-sectional area needed to calculate stress was measured from brightfield micrographs taken at x2.5 magnification on an Olympus SZX7 stereomicroscope (Olympus, Tokyo). Alongside this, strain was measured optically using a video extensometer approach (Fig 3.01). Following this, stress-strain curves were constructed, and in accordance with ASTM E8, the Elastic modulus (E), Yield Strength (σ_{yield}) and Failure Strain ($\epsilon_{failure}$) were calculated [149]. Using this standard σ_{yield} was calculated using the 0.2% offset approach. Here a line is offset from the elastic region of the stress-strain curve by 0.2% strain. Subsequently, the σ_{yield} is calculated from the intercept of the stress-strain curve and the plotted line. Although a hysteresis loop may be a more accurate method of determining the true onset of plasticity, the 0.2% strain approach is more practical for delicate samples and is within the scope of ASTM and ISO standards.

The fatigue properties of micro-strut samples were also measured. These tests were conducted on a TA Instruments test bench system (Waters, Milford, MA) using a 200N load cell. A tension-tension (R=0.1) test configuration was followed, with cyclic loading at 50Hz under load control. These tests were carried out at percentages of the yield strength (80, 65, 50, 35, 25 and 20%). S-N curves were constructed by noting the number of cycles to failure at each load level. In the absence of failure runout was recorded at $N = 10^7$ cycles.

Lattice samples were also subjected to compression testing. Tests were performed on an Instron 8801 testing system (Instron, Northwood, MA) equipped with a 100kN load cell, under displacement control at a strain rate of 0.5%/s. Cross-sectional areas needed for stress calculations were measured using a callipers. Strain was measured via crosshead displacement. Stress-strain curves were constructed, and in accordance with ISO 13314 the toe regions were removed [152]. Following this E, σ_{yield} , and the Ultimate Compressive Strength (UCS) were calculated similarly to tensile testing.

3.2.5.1 Mechanical testing – optical strain measurements

In order to optically record strain during tensile testing, two markers were painted on the sample gauge sections using a needle tip (Fig 3.01.g). Tests were then recorded using a DinoLite digital microscope (Dino-Lite Digital Microscope, Torrance, Ca) at a frequency of 10 frames/s. Subsequently, the digital image series was analysed in MATLAB to calculate strain. However, before strain measurements were calculated, the digital image series was linked to the force data. This was achieved by finding the frame in which fracture

occurred in, and using it as a reference. The strain was then measured throughout the image series by calculating the relative distance (in pixels) between the two markers. A loess curve with a weight of 0.01 was fitted to the data and strain was trivially calculated. The location of each marker was determined by identifying its centroid after an image filtering and thresholding operation (Fig 3.01.b to 3.01.d).

To validate this method, further tensile testing was conducted for comparison of this method against extensometer readings. Here, dog-bone samples were machined from wrought Ti6Al4V, Grade 23 to the specifications of ASTM E8 cylindrical specimen no.4. Subsequently, samples were pulled to failure in uniaxial tension on an Instron 8801 hydraulic testing system (Instron, Northwood, MA). This was carried out under displacement control at a strain rate of 0.5 %/s. Force was measured with a 10kN load cell and strain was measured with both the proposed video extensometer and a contact extensometer approach. The stress-strain curves for each approach were closely matched (Fig 3.01.e). Furthermore, as assessed by strain at; the yield, ultimate tensile strength, and failure, there is also no significant difference between the two approaches (Fig 3.01.e).

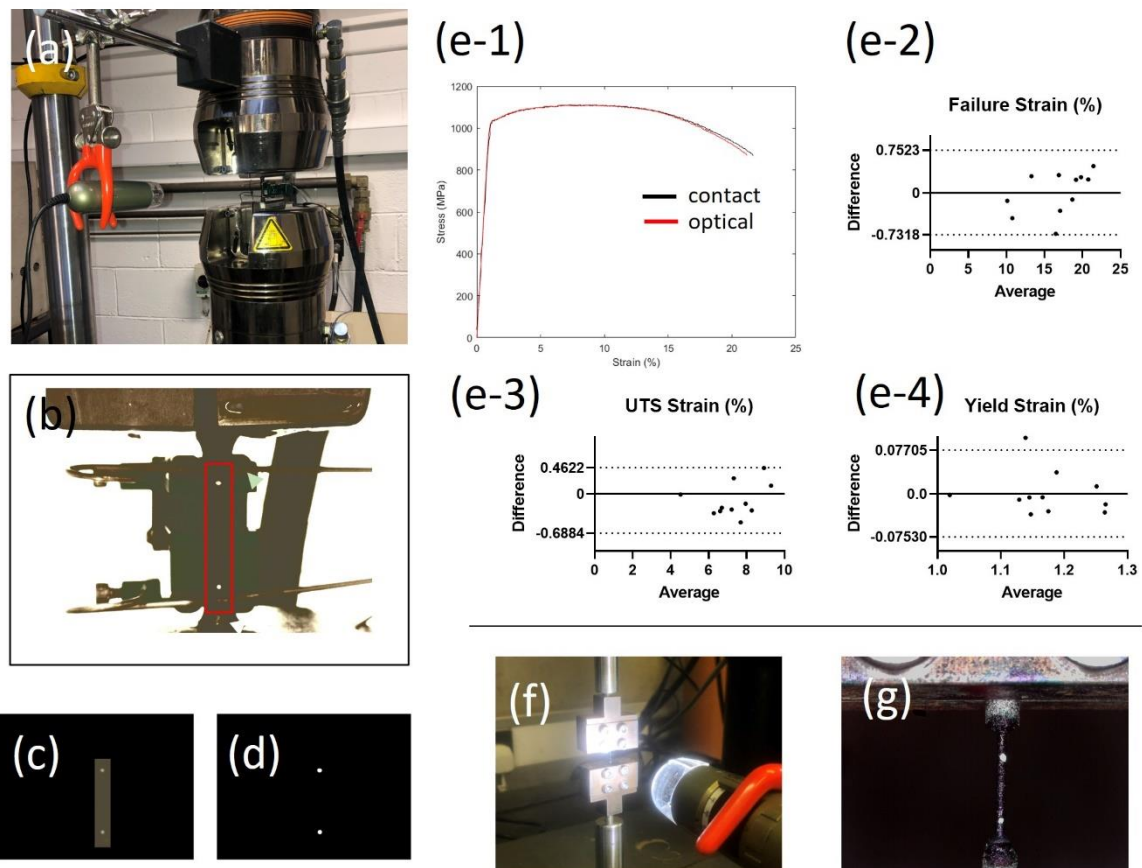


Figure 3.01. The video extensometer approach was compared to a contact extensometer approach for measurements of strain. (a) Both approaches were used to measure strain on full size dog-bone samples. (b to d) The basic image processing steps for the video extensometer are shown; (b) The

field of view is narrowed down to the gauge region using a ROI. (c & d) The marker locations were measured by processing the ROI with (c) a thresholding technique and (d) a binary operation. (e-1) Representative stress strain curve generated using the video extensometer approach (red) and the contact extensometer approach (black). Band Altman plots for (e-2) failure strain, (e-3) ultimate tensile strain and (e-4) failure strain. (f & g) The video extensometer approach applied to micro-strut samples is also shown.

3.2.6 Scanning electron microscopy

Characterisation of fracture surfaces was assessed using SEM. Images were taken using the SE2 detector on a Zeiss ULTRA SEM microscope (Carl-Zeiss-Stiftung, Heidenheim, Germany) with a 60µm aperture, 15kV excitation voltage and 12mm working distance.

3.2.7 Statistical analysis

Statistical tests used to compare groups are indicated in figure legends. Significance was accepted at a level of $p < 0.05$. Results are expressed as mean $\pm$ standard deviation. This analysis was performed in GraphPad Prism statistical analysis software (GraphPad, La Jolla, Ca).

3.3 Results and discussion

3.3.1 Bulk processing parameters are not optimal for micro-strut lattices

Due to the full melting mechanism employed in SLM, porous defects arise as a result of poorly chosen process parameters [142], [144]. In general, this relationship is described by the energy density input, which under ideal circumstances induces a stable pool of melted material, adequately fused to the underlying substrate upon solidification [142], [144]. Among the process parameters that contribute to the energy density input, laser exposure time describes the dwell time per point distance in pulsed wave emission based SLM [47], [153] [47], [153].

From 2-D porosity analysis, it is apparent that a wide window of printing parameters are suitable for processing bulk (large) objects (Fig 3.02.a). Relative density is maintained across the full range of parameters investigated; however, a small number of porous defects can be observed at a laser exposure time of 264µs. These defects are characteristic of gas entrapment pores, introduced into the sample by turbulent melt pool dynamics, a consequence of an excessive energy density input. This is indicative of the extent of the suitable processing window, beyond which further gas entrapment and associated keyholing defects are likely to emerge.

It is also apparent that the window of suitable processing parameters for bulk materials does not translate to the micro-strut lattice samples. While a defect free surface is

maintained in the bulk material at low exposure times, a high frequency of large porous defects can be observed in the micro-strut samples (Fig 3.02.b). These defects are characteristic of lack of fusion (LOF) pores, introduced into the sample by incomplete melting, a consequence of a low energy density input [142], [144]. A number of studies have observed a similar increase in the frequency of these defects as feature size is reduced, suggesting a higher energy density input may be required for micro-strut processing [146], [147]. Consequently, it is unsurprising that both the defect size and frequency in the micro-struts is reduced as laser exposure time is increased from 33 μ s to 132 μ s (Fig 3.02.c). Beyond 132 μ s, the frequency of defects begins to increase. In the micro-strut samples, gas entrapment and large keyhole defects begin to emerge, and are indicative of an excessive energy density input [142], [144]. By 264 μ s, similar defects can also be observed in the bulk material, albeit to a minimal extent, and not substantially compromising to the relative density. Consequently, a much smaller window of suitable process parameters is available for micro-strut fabrication.

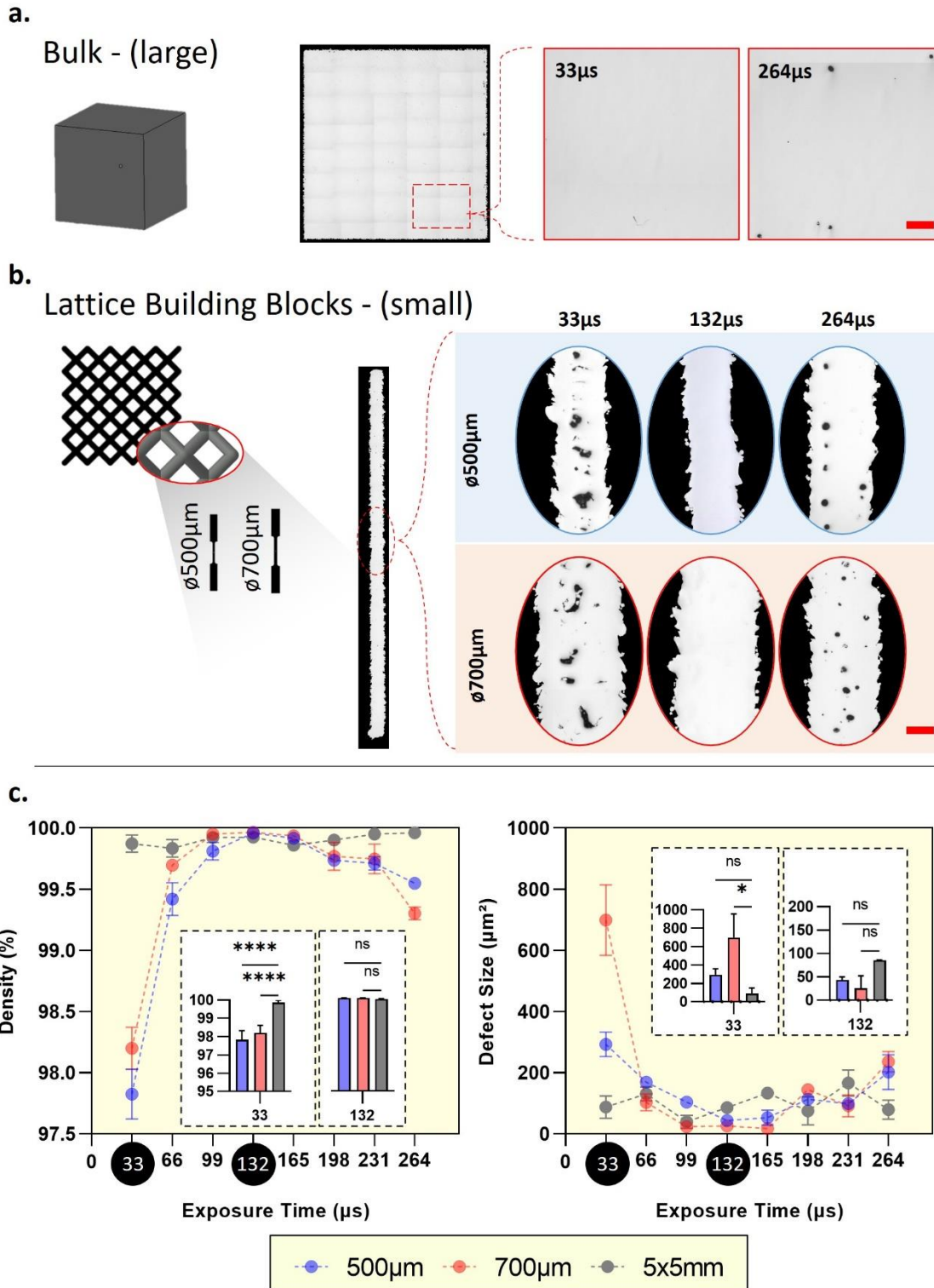


Figure 3.02. **Bulk processing parameters are not suited for micro-strut lattices.** c.) Across the range of parameters suitable for processing bulk material, only a small window is suitable for processing micro-struts with good material density. b.) Below this window, micro-strut cross sections exhibit 1.) Large LOF defects, indicating energy density is too low, and 2.) gas entrapment and keyhole defects, indicating energy density is too high. This is contrary to a.) the bulk material, which exhibits good density across the full range of parameters investigated. All error bars denote standard deviation. *, **, *** and **** denotes

statistically significant differences ($p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, one-way ANOVA). All scale bars (red) are equal to $100\mu\text{m}$.*

Porous defects inherited from the fabrication process are well understood to have a detrimental effect on mechanical properties. If their volume percentage is small, the effect of gas entrapment and keyhole type defects is negligible [143], [144]. In such instances, microstructural and non-porous surface defects drive higher stress concentrations and consequently dominate failure mechanisms. On the contrary, the effect of LOF defects is apparent even at low volume percentages; this is largely driven by a reduction in load bearing capacity around the irregular pore morphology [81], [143], [144].

In this work, a size effect can be observed in the frequency of LOF defects between bulk and micro-strut samples. While a defect free surface was maintained in the bulk material across the full range of parameters investigated, a high frequency of these defects can be observed in the micro-strut samples at lower energy density inputs. To investigate this further, the thermal history from SLM processing was considered using computational modelling (Fig 3.03). In bulk and micro-strut samples, predicted temperature profiles were extracted at the centremost point along the C&H scan tracks. As the laser progresses across the computational domain, it is unsurprising that a peak temperature is predicted as the centre of the melt pool passes through this point ($t = 0\text{s}$). A size effect is also apparent, whereby a lower peak temperature is predicted in the micro-strut samples. Similar feature size dependent behaviour has been observed in the literature, and is largely attributed to faster rates of heat loss on account of an increased surface to volume ratio as feature size is reduced [145], [150]. Below a critical threshold for turbulent melt pool dynamics, lower peak temperatures coincide with smaller melt pool dimensions, and consequently with the higher frequency of LOF defects in the micro-strut samples [154].

Pre and post heating effects are also apparent as the laser traces both preceding ($t < 0\text{s}$) and succeeding ($t > 0\text{s}$) scan tracks. The resultant peaks in temperature are separated on a time-scale equal to the length of each successive pass by the laser. Consequently, the thermal profile in the micro-strut samples is highly localised, whereas in the bulk material, thermal peaks are more distinctive, separated by much longer scan tracks.

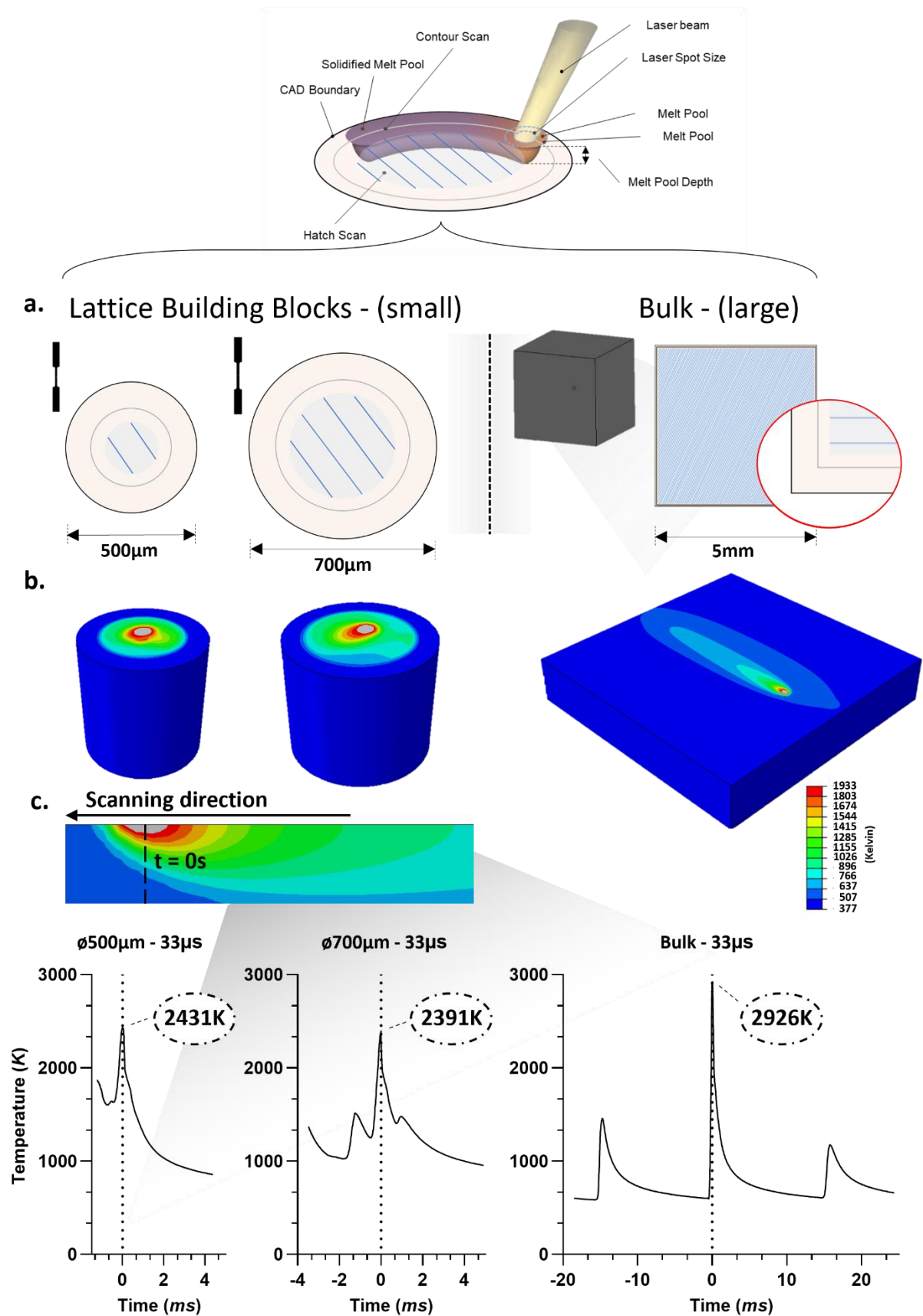


Figure 3.03. **Computational models indicate lower processing temperatures in micro-struts.**
a.) C&H laser scanning tracks for each design. b.) Laser scanning of C&H tracks was simulated in the finite

element solver Abaqus with a DFLUX subroutine. c.) Higher melt pool temperatures were observed in the bulk material than in the micro-struts.

3.3.2 Implementing feature size specific processing parameters improves micro-struct mechanical properties

We next assessed the effects of implementing feature size specific parameters for defect minimisation on the mechanical properties of micro-struts in uniaxial tension (Fig. 3.04). Here, significant improvements in mechanical properties could be observed using optimised printing parameters (exposure time of $132\mu s$) compared to those developed for bulk materials (exposure time of $33\mu s$). This extended to both the $\varnothing 500\mu m$ and $\varnothing 700\mu m$ struts, with changes observed in the elastic modulus, yield strength and failure strain (Fig 3.04.c).

It is well understood that LOF pores are particularly detrimental to the mechanical properties of parts produced by SLM [81], [143], [144]. During elastic deformation, this is largely attributed to a reduction in the effective load bearing cross-sectional area; a consequence of the large and irregular pore morphology [81]. This effect extends to both the elastic modulus and yield strength. In this study, a high frequency of LOF defects was apparent in the micro-strut samples at lower energy density inputs ($33\mu s$). These defects account for a large portion of any given cross-section, and consequently, it is unsurprising that optimisation of relative density is accompanied by increased stiffness and yield strength. For example, the yield strength of the $\varnothing 500\mu m$ and $\varnothing 700\mu m$ samples increased by 37.44% and 46.59% respectively compared to samples manufactured using suboptimal parameters.

From the stress-strain curve, it is apparent that both groups continue to deform plastically after yielding (Fig 3.04.b). In ductile materials, stress typically continues to increase after the yield point. This continues up to the ultimate tensile strength (UTS), at which necking occurs and a state of triaxial stress is induced. During this process, micro voids begin to nucleate, which grow and coalesce eventually forming large cracks [80], [81]. As these cracks grow, a less ductile shearing failure is eventually induced. This occurs along the axis of maximum principal stress i.e. 45° degree inclination to the load direction [80], [90]. The presence of LOF pores accelerates this process, largely driven by the existing state of stress around the irregular pores [80], [81]. Consistent with such reports, we observed that loading beyond the UTS is associated with less ductile failure, and a much lower strain to failure in micro-struts produced using suboptimal processing parameters.

It can also be observed that the $\varnothing 700\mu m$ strut exhibits improved mechanical properties compared to the $\varnothing 500\mu m$ strut. This is apparent both before and after parameter

optimisation. Although not the primary focus of this study, it is indicative of size effects beyond porosity. These effects are understood to be derived from additional feature-size dependent factors, inherited from the fabrication process. This extends to microstructure and surface roughness [71], [141], [145].

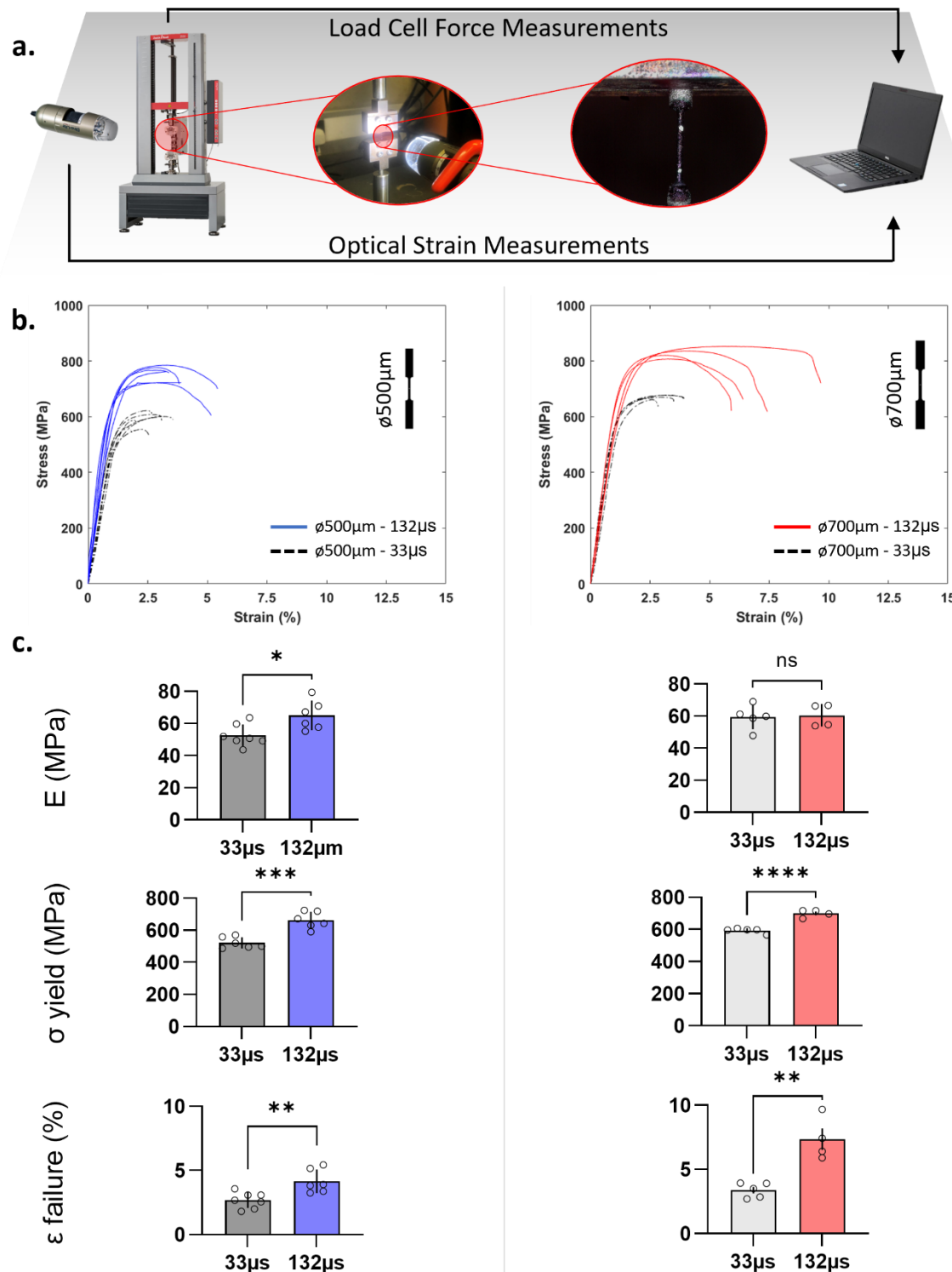


Figure 3.04. Feature size specific processing parameters yield improved tensile properties in micro-struts. Micro-Struts were fabricated with 2x sets of processing parameters; 1.) suitable for bulk

material (33 μ s) and 2.) suitable for micro-struts (132 μ s). a.), b.) They were then pulled to failure in uniaxial tension under displacement control. c.) Improvements in elastic moduli, yield strength, and failure strain could be observed in groups fabricated with the set of processing parameters suitable for micro-struts (132 μ s). All error bars denote standard deviation. *, **, *** and **** denotes statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, student's t -test).

SEM was next used to assess the mode of fracture (Fig 3.05). These results coincide with observations made during tensile testing (Fig 3.04) and point to a more ductile failure after optimising relative density. Consistent with the 2D porosity analysis (Fig 3.02), large LOF pores are visible in the 33 μ s group, and have a clear influence on the mode of failure. Here, multiple shear planes can be seen originating from the complex multi-faceted pore architecture [80], [148]. On the contrary, the 132 μ s group appears fully dense. This is accompanied by more ductile failure in the 132 μ s group. This is characterised by a ductile region of micro-void coalescence normal to the tensile axis (Region I), progressing into a less ductile region of shear failure normal to the axis of maximum principal stress (Region II) [80], [141].

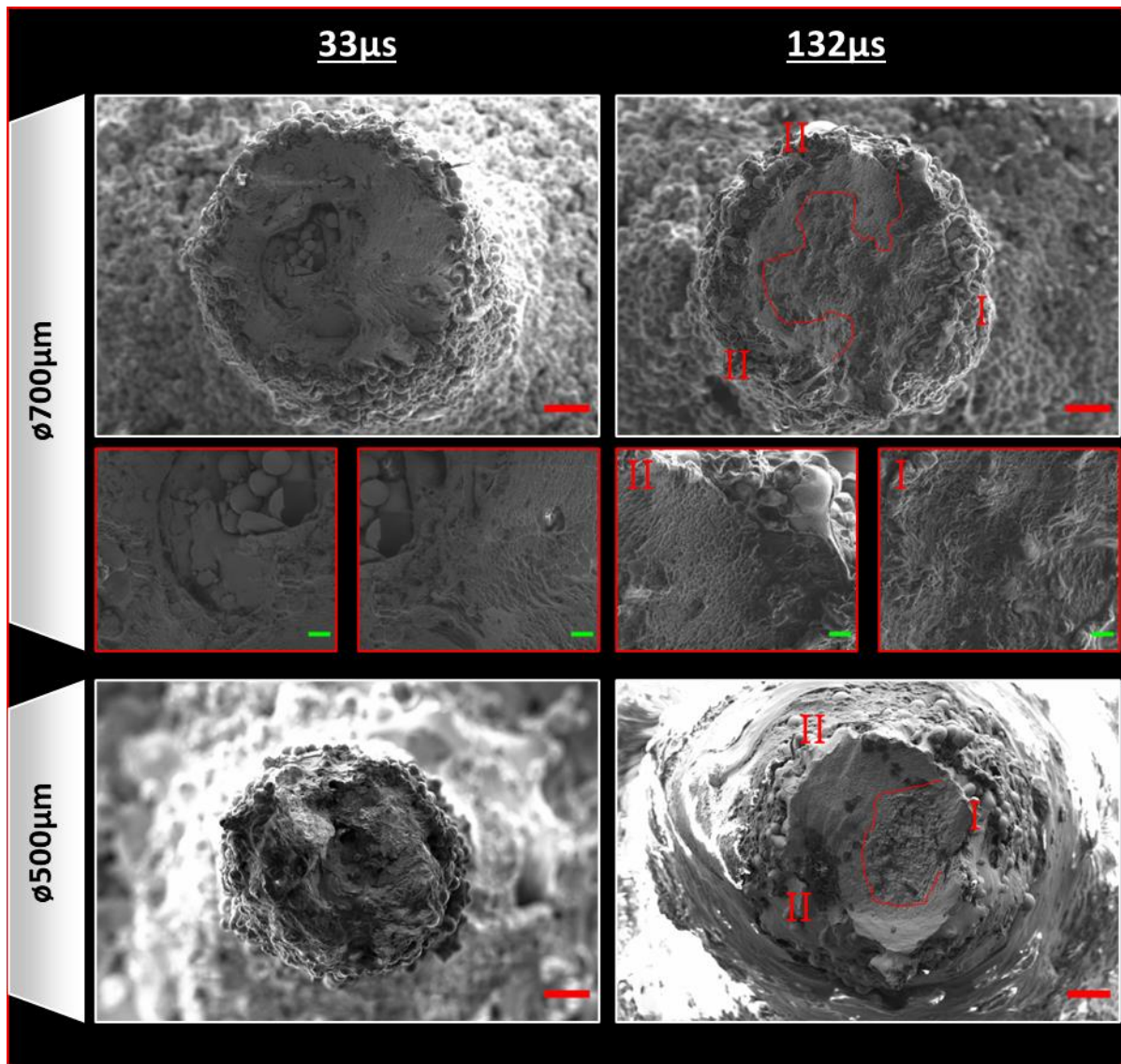


Figure 3.05. **Fracture surfaces coincide with Improved tensile properties.** SEM showing representative fracture surfaces for groups fabricated with 33μs (Left), and 132μs (Right). Large LOF pores are visible in the 33μs group, along with comparably brittle fracture with multiple shear planes originating from the complex multi-facet pore architecture. In contrast, the 132μs group exhibits a fully dense fracture surface, along with increased signs of ductility; with failure processing from a ductile region of micro-void coalescence (I), progressing into a more brittle shearing mode (II). Scale bars are equal to 100μm (red), and 20μm (green).

3.3.3 The influence of processing parameters on the fatigue properties of micro-structs

The mechanical properties of the micro-strut samples were also assessed in fatigue. The fatigue resistance of SLM manufactured components is typically determined by defects in the material, which act as critical sites for crack nucleation [81], [155]. Here, the fatigue properties were measured before and after the optimisation of micro-strut relative density (Fig 3.06.b & 3.6.c). S-N curves were constructed for the absolute stress, but also

normalised as percentages of the yield strength (Fig 3.06.c). As different yield strengths were measured in each group, this allowed us to capture the entire range of fatigue properties, spanning from low cycle fatigue (LCF) to high cycle fatigue (HCF).

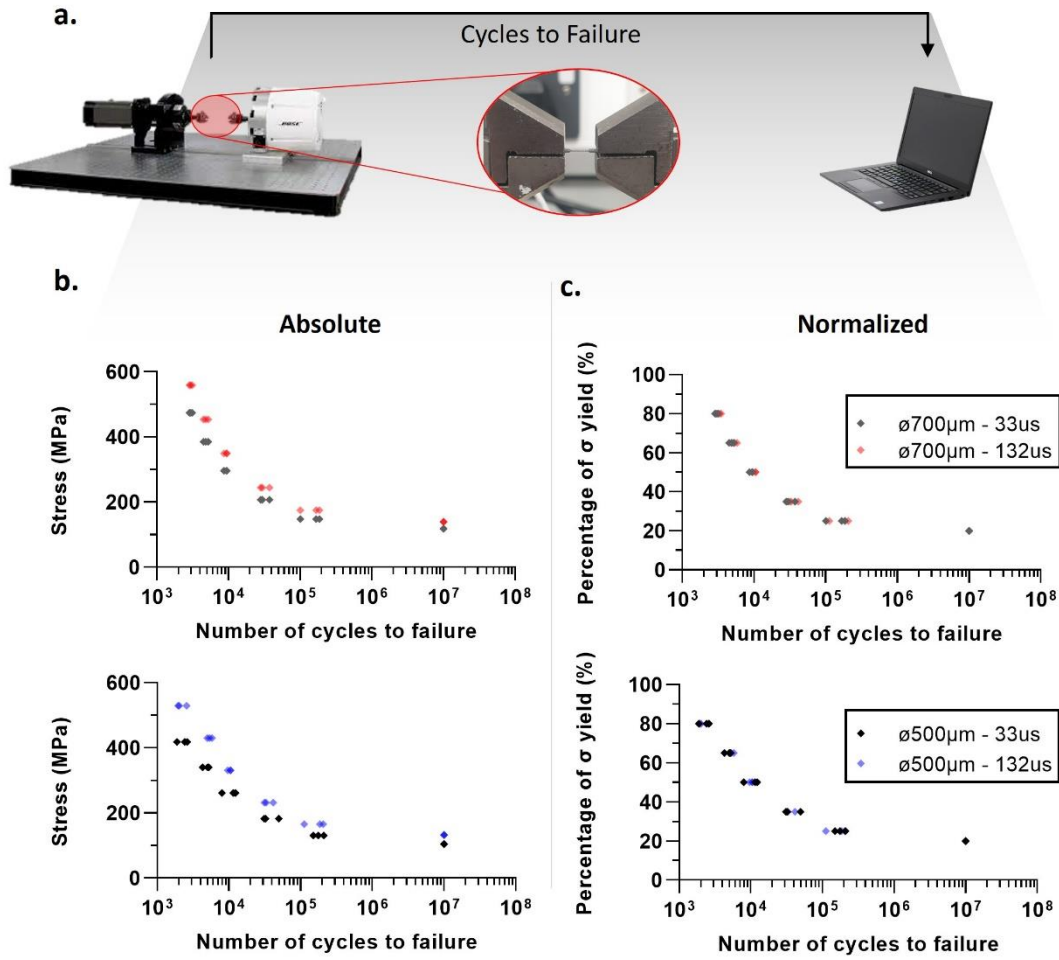


Figure 3.06. Feature size specific processing parameters yield no apparent improvement in fatigue properties. a.) Micro-struts were tested in load-controlled tension-tension fatigue at 80, 65, 50, 35, 25, and 20% of the tensile yield strength. The number of cycles to failure was recorded, and plotted against load creating S-N curves. b.) Plotted against absolute stress, the 132 μ s group exhibits a higher number of cycles to failure at any given load. c.) When stress is normalised to account for differences in tensile strength, samples processed at 33 μ s and 132 μ s behave similarly.

In general, fatigue data is normalised to the yield strength [102], [156], [157], [158]. This is necessary for comparison of the between distinctive LCF damage and HCF damage. LCF is characterised by the application of a high stress relative to the yield strength, and subsequently results in a short number of cycles to failure [101], [102]. Under these conditions, both the 33 μ s and 132 μ s groups exhibit a similar number of cycles to failure. This can also observed as the loading regime progresses into HCF, which is characterised by the application of a lower stress relative to the yield strength, which results in a larger number of cycles to failure [101], [102]. Consequently, it is apparent that porous defects

do not significantly impede the fatigue properties of micro-strut samples beyond the effects of yielding. This can be related to the energy needed to initiate a crack. From SEM, it is clear that fatigue cracks generally nucleate from stress concentrations around surface or near surface defects (Fig 3.07) (the potential sites of the critical crack nucleation are marked with a green arrow). These defects are inherited from the fabrication process and are primarily a consequence of partially adhered powder [64], [71], [72], [159]. Due to their surface free energy, they typically experience high stress intensity factors (SIF) [110], [160]. Consequently, critical crack propagation is most likely to occur close to the surface.

In agreement with the 2D porosity analysis, large LOF defects are clearly visible in the $33\mu\text{s}$ group. Despite no obvious impact to the overall fatigue life (normalised to the material yield strength), these defects clearly disrupt the progression of the crack through the crack growth zone (Region I) (Fig 3.07). After crack nucleation, fracture toughness describes the material's ability to resist further crack growth. This is derived from local material properties at the crack tip, and consequently limited by LOF voids [81]. As this was also apparent in tensile yielding, it is more appropriate to consider these effects before the normalisation of the S-N curves (Fig 3.06.b). Unsurprisingly, the $132\mu\text{s}$ group exhibits a slight increase in the number of cycles to failure. Despite this, the achievable fracture toughness of titanium alloys is low, and generally, the crack initiation phase dominates the prediction of overall fatigue life [161]. As cracks generally nucleate from surface defects in this study, the effect of porosity is only marginal.

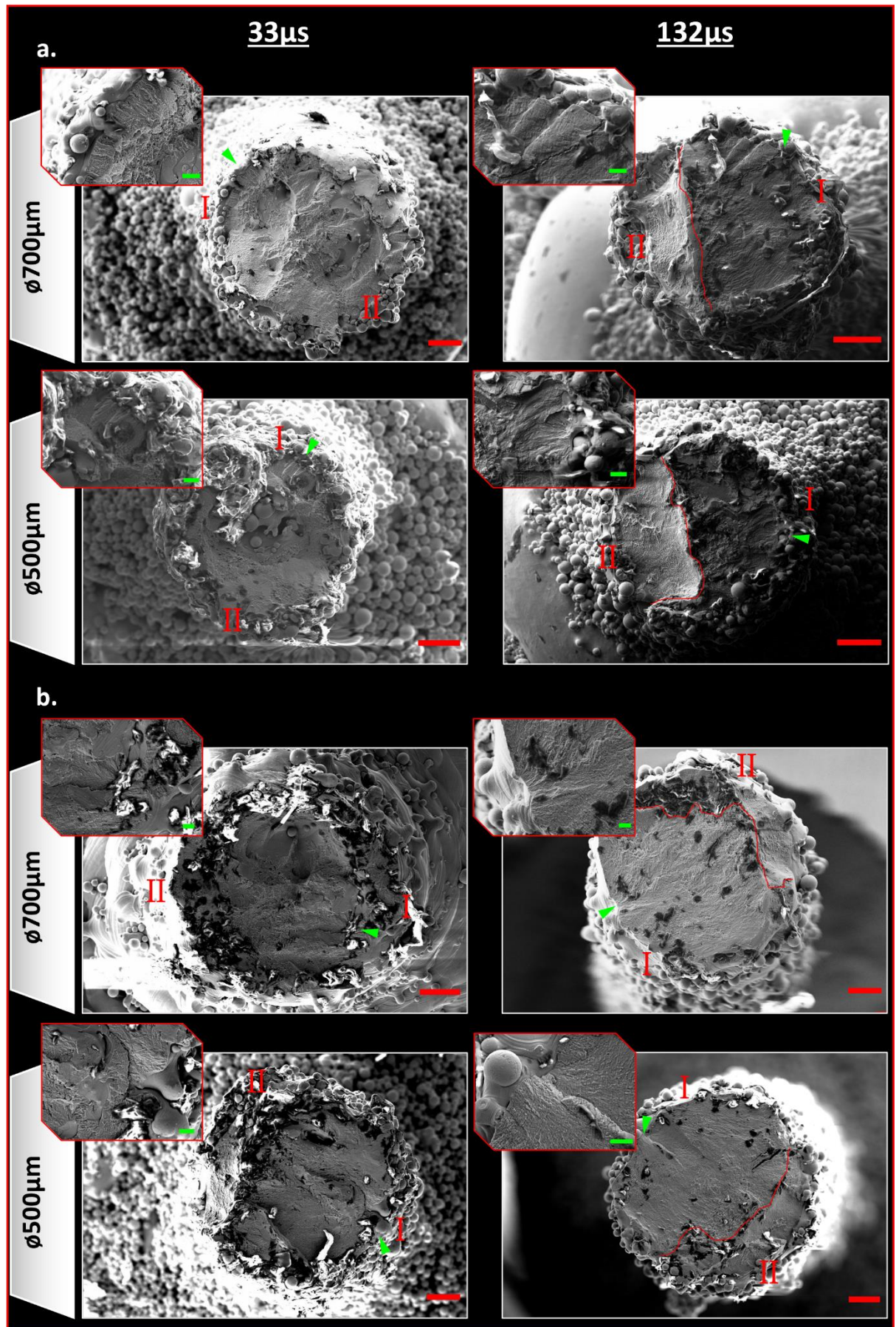


Figure 3.07. Cracks initiate in surface and near-surface defects, regardless of internal porosity. SEM showing representative fracture surfaces for groups fabricated with 33 μ s (Left), and 132 μ s (Right). Large LOF pores are clearly visible in the 33 μ s group, while the 132 μ s group appears fully dense. Despite this, crack initiation can be generally located in surface defects in both a.) LCF, and b.) HCF fatigue loading regimes. Potential sites for crack initiation are indicated by a green arrow, and magnified (top left). Where possible, the crack growth, and final fracture zones are labelled Regions I and II respectfully. Scale bars are equal to 100 μ m (red), and 20 μ m (green).

3.3.4 The influence of processing parameters on the mechanical properties of full lattice structures

Parameter optimisation was also applied to full lattice structures. Consequently, the mechanical properties were assessed in compression (Fig 3.08). It is important to note both the lattice design and the material properties contribute to these properties. However, as the lattice design was kept constant, improvements in material properties could be inferred.

For both 33 μ s and 132 μ s groups, mechanical failure can be observed on the stress-strain curves as a loss in strength after the UTS (Fig 3.08.b). This can be associated with the formation of a shear band, orientated 45° to the loading direction (Fig 3.08.d). This is typical of BCC lattices, and attributed to the localisation of severely deformed struts to a given plane [162], [163]. Due to the symmetry of the BCC unit cell, this usually occurs 45° to the loading direction. Despite similar failure mechanisms, the mechanical properties of the lattice generally improve after parameter optimisation. The 132 μ s group exhibits a higher stiffness than the 33 μ s group. The effect of porosity is known to be much less detrimental under compressive loading than it is under tensile loading. This is a consequence of the closing of pores, rather the opening of them. However, in the BCC lattice, struts are under tensile and shear loading, rather direct compression [81], [143], [144]. Consequently, the reduction in stiffness in the 33 μ s group can be related to the proportion of material that is load bearing. Due to the higher density of defects in the as-built lattice, a larger proportion of the material is non-load bearing, which results in a decreased elastic modulus. For the same reason, significant improvements in the yield strength and UTS were also observed after parameter optimisation.

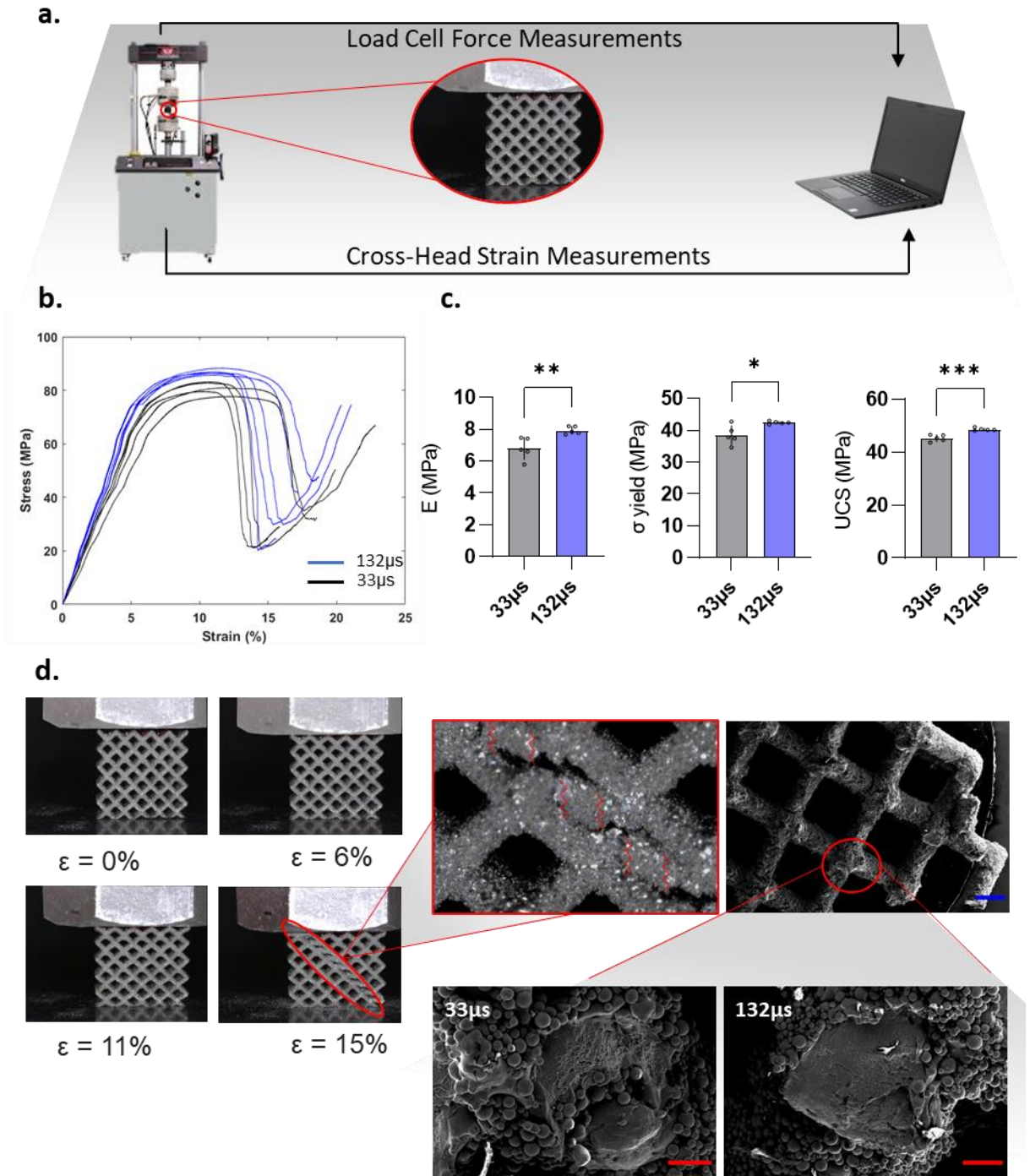


Figure 3.08. Processing Parameters Influence the Mechanical Properties of Full Lattices. Lattices were fabricated with 33 μ s and 132 μ s exposure times. a.), b.) They were then compressed uniaxially under displacement control until collapse. c.) Improvements in elastic moduli, yield strength, and ultimate compressive strength could be observed in groups fabricated with the set of processing parameters suitable for micro-struts (132 μ s). All error bars denote standard deviation. *, **, and *** denotes statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$ and *** $p < 0.0002$, student's t -test). d.) Fracture surfaces coincide with improved compressive properties. Similar to micro-strut fracture surfaces, large LOF pores are visible in the 33 μ s group, whereas the 132 μ s group appears fully dense. Scale bars are equal to 100 μ m (red), and 1mm (blue).

3.4 Conclusion

This work investigated the influence of feature size on defect formation in SLM manufacturing. In doing so, a range of suitable printing parameters was identified for processing micro-strut lattices with high relative density and improved mechanical properties. By using micro-strut dog-bone samples, the geometric design of a specific lattice was not a factor, allowing us to characterise the properties of the bulk material.

We found that the window of suitable processing parameters for printing micro-strut lattices was much smaller than it was for bulk objects. At lower energy densities inputs, a high frequency of LOF defects could be observed in micro-strut samples, while at high energy density inputs an increased frequency of gas entrapment and keyhole defects could be observed. On the contrary, the bulk samples maintained high relative density across most of this range. As gas entrapment and keyhole defects were below 1% in the micro-struts samples, we decided to focus on the effects of the LOF defects, which even at a low volume percentage can have a dramatic impact on mechanical properties.

From computational modelling, it was apparent that the increased frequency of LOF defects was a consequence of higher rates of heat loss due to an increased surface to volume ratio. Consequently, a higher energy density input was required for optimal processing of micro-struts.

The minimisation of porous defects using optimised processing parameters was accompanied by improved mechanical properties in both tension and compression. Improvements in strength and stiffness were largely attributed to an increase in the percentage volume of load bearing material, while improvements in failure strain were largely driven by the minimisation of stress concentrations around the irregular pore morphologies. Porous defects did not significantly impede the fatigue properties of micro-struts beyond the effect of yielding. From SEM, it was apparent that crack initiation was dominated by surface defects, which on account of their surface free energy, experienced a much higher SIF.

Chapter 4: Morphological and microstructural characteristics of additively manufactured Ti-6Al-4V micro-struts determine feature size dependent tensile and fatigue properties

This chapter is currently being prepared for submission to a peer reviewed journal, under the title ‘Morphological and microstructural characteristics of additively manufactured Ti-6Al-4V micro-struts determine feature size dependent tensile and fatigue properties’, and is co-authored by Conor O’Keeffe, Arnie Sasnauskas, Harry Shipley, David Taylor, Caitríona Lally and Daniel J Kelly.

EBSO scans were performed on polished samples at the Muyan R&D Centre, China. A, S wrote the MATLAB code for analysis of the EBSO scans, utilising the MTEK toolbox. H, S provided expert opinion on printing strategies. D, T provided expert opinion on fracture mechanisms. C, L and D.J, K supervised this work.

Abstract

Despite the many advantages of the powder bed fusion (PBF) additive manufacturing technique, defects inherited from the fabrication process can result in a degradation of mechanical properties. These defects are often inherited disproportionately in small diameter micro-struts, and consequently have a more detrimental impact on the mechanical properties of lattice structures. These effects have been correlated to a range of process inherited characteristics. However, due to lack of systematic studies, their proportional contribution towards the underlying mechanisms of deformation and failure is unclear. In this study, the mechanical properties of Ti-6Al-4V micro-struts fabricated using PBF were investigated as a function of strut diameter. A decrease in yield strength under tensile loading in smaller diameter struts, as well as a diminished resistance to crack growth under fatigue loading, suggested a feature size dependent resistance to plasticity. These changes in mechanical properties correlated with a reduction in the proportion of load bearing material relative to non-loading bearing surface defects in any given cross-section. Consequently, after normalisation of stress to measurements of the effective load-bearing area, these effects were no longer apparent. Beyond the effects of morphology, an increasingly brittle mode of failure could be observed under tensile loading as feature size was reduced. Here a transition towards cleavage fracture indicated that microstructural changes were also a factor in determining the mechanical response. This could be correlated to an increase in crystallographic texture, and favourable alignment towards low energy slip systems.

4.1 Introduction

Powder bed fusion (PDF) additive manufacturing techniques have enabled the fabrication of geometrically complex metallic lattice structures [11], [43]. Despite the many advantages of this approach, the mechanical properties of the individual struts making up these lattices can be significantly different to the bulk material [15], [76], [111], [164], [165], [166]. In fact, the mechanical properties of these micro-struts exhibit feature size dependent behaviour, which is notable by only small changes in the strut diameter [15], [76], [164], [165], [166]. This is largely a consequence of the compromising effect of process inherited defects, which are inherited disproportionately in small diameter struts [15], [76], [164], [165], [166].

Among these defects, porous inclusions may arise as a consequence of non-optimal laser processing parameters, which are known to contribute to reduced strength and failure strain [81], [143]. A number of studies have also observed an increase in the frequency of such defects as feature size is reduced [147], [148], [164]. We have previously shown this is largely a consequence of increased rates of heat loss on account of larger surface-to-volume ratios in small diameter struts. Fortunately, these effects can be alleviated using feature size dependent processing parameters [142], [144]. However, process inherited defects extend beyond porosity, and consequently, feature size dependent mechanical properties have remained an issue in studies reporting optimised relative density [15], [165]. In this regard, a number of studies have reported the effects of surface roughness, which in PBF is commonly inherited in the form of partially adhered powder [15], [111], [165]. Furthermore, these defects are largely unavoidable due to the physics of the melt pool, along with powder granule size and morphology [64], [71]. Generally, these near-surface defects control the fatigue resistance of SLM manufactured components. This is a consequence of high stress intensity factors (SIF), which they experience due to their surface free energy [24], [101], [110]. In tension they can modify the development of local plasticity, resulting in reduced ductility. In small diameter struts, surface defects can account for a significant portion of the strut diameter, and consequently lead to a new class of irregularity described as morphological [71], [111], [166], [167], [168], [169], [170]. As a result, large variations in cross-sections may develop along the length of a strut, which can negatively impact mechanical properties by reducing the effective load bearing capacity.

Beyond the effects of surface roughness, it is well established that the microstructure inherited through PBF fabrication has a significant effect on the mechanical properties of titanium alloys [15], [134]. As a consequence of the layer wise nature of SLM, and the large temperature gradients during solidification, an array of columnar body centered cubic (BCC) β grains are usually formed through epitaxial growth [126]. Following this, rapid

cooling below the martensite start temperature drives a decomposition towards the more brittle, hexagonal close packed (HCP) α' martensite, composed of thin α' -laths within the prior β grains [126], [134], [171]. Typically, the final microstructure is characterised as predominantly α' martensite, with small amounts remaining $\alpha+\beta$. However, in small diameter struts, the rate of cooling is enhanced by an increased surface-to-volume ratio, and entirely α' martensite grain structures are commonly observed [15], [171]. Furthermore, precipitation of the α' -laths is limited as cooling rates are increased, and consequently, lath thickness typically appears more refined as feature size is reduced [15], [76], [134]. In accordance with the Hall-Petch effect, these effects can, in turn, drive more brittle behaviour in small diameter struts [15], [76], [134]. In addition to α' -lath thickness, the crystallographic orientation of each grain to a preferred crystallographic slip system will promote dislocation movement and plastic flow [128], [129]. In SLM, the α' phase generally exhibits an inherently weak texture, which can be attributed to the high number of variants that precipitate within each columnar β grain [126], [172].

Although the existence of such process inherited factors is understood, their impact on the feature size dependent mechanical properties of titanium micro-struts remains unclear and contradictory findings are often reported in the literature. For example, a decrease in strength has been commonly observed as strut diameter is decreased, which is generally associated with a degradation of morphology [164], [166]. On the other hand, an increase in strength has also been observed in smaller diameter struts, and largely attributed to microstructural refinements [15], [76]. From a design perspective, a lack of systematic studies has made it difficult to decompose the proportional contribution of these factors; these are essential for predicting mechanisms of deformation under loading. Furthermore, the resulting fracture surfaces have not been studied alongside these trends, which has contributed to our lack of understanding of the proportional contributions of these factors towards failure mechanisms. Therefore, the objective of this study is to decompose the contribution of morphological and microstructural inherited factors towards deformation and failure mechanisms in small diameter Ti-6Al-4V struts in tension. This study will also be extended to include fatigue properties, which to the best of our knowledge has not been studied as a function of strut diameter.

4.2 Methods

4.2.1 Design & manufacturing

Micro-strut samples were designed using the computer-aided-design (CAD) software Autodesk Inventor (Autodesk, San Francisco, Ca), as cylindrical dog-bones of various

gauge diameters ($\varnothing 300$, 500 and 700 μm) with dimensional ratios proportional to ASTM E8 [149].

Samples were fabricated using a selective laser melting (SLM) PBF approach, on a Realiser SLM 50 manufacturing system (spot size = 160 μm) (DMG MORI, Bielefeld, Germany), from Ti6Al4V, Grade 23 powder (particle size = 10-45 μm). Samples were built in slices of 0.25 μm , for which a contour-and-hatch (C&H) laser scanning strategy was adopted, with processing parameters taken from Chapter 3.

Following printing, electrical discharge machining (EDM) was used to remove the samples from the build plate. Finally, loose powder was removed by sonication in isopropyl alcohol for 30 minutes.

4.2.2 Mechanical testing

Tensile tests were carried out on micro-strut samples. Here, samples were pulled to failure under uniaxial tension, under displacement control, and at a strain rate of 0.5%/s. These tests were conducted on a Zwick universal testing machine (Zwick Z005, Zwick GmbH & Co. Ulm, Germany) (Fig 4.01.a). Force was measured using a 200N load cell, and converted to stress using measurements of cross-sectional area. Here, the gauge section cross-sectional areas were imaged at x2.5 magnification on an Olympus SZX7 stereomicroscope (Olympus, Tokyo). From these images, the average strut thickness along the gauge section was measured in Matlab (MathWorks, Cambridge, UK). Strain was measured optically using a video extensometer approach (Fig 4.01.a), further described in Chapter 3. In accordance with the ASTM E8 standard for mechanical testing of metallic materials, Elastic modulus (E), Yield Strength (σ_{yield}) and Failure Strain ($\epsilon_{failure}$) were calculated for each sample from the stress-strain data (Fig 4.01.b) [149].

Mechanical testing of the micro-strut samples was extended to fatigue properties. These tests were carried out under load control, at 80, 65, 50, 35, 25 and 20% of the yield strength (acquired from the tensile tests). These tests were conducted at 50Hz under tension-tension ($R=0.1$), using a 200N and a TA Instruments test bench system (Waters, Milford, MA) (Fig 4.03.a). For each loading level, S-N curves were constructed by noting the number of cycles to failure at each load level. In the absence of failure, runout was considered at $N = 10^7$ cycles.

4.2.3 Scanning electron microscopy

Characterisation of fracture surfaces was assessed using scanning electron microscopy (SEM). Images were acquired on a Zeiss ULTRA microscope (Carl-Zeiss-Stiftung,

Heidenheim, Germany) which was equipped with a SE2 detector. These images were acquired using a 60 μ m aperture, 15kV excitation voltage and 12mm working distance.

4.2.4 Surface roughness measurements

Surface roughness was characterised along the z-axis of the micro-strut gauge sections. The profile of each sample was acquired at x50 magnification using a Filmetrics Profilm 3D white light interferometry (WLI) (KLA Instruments, Milpitas, Ca). This data was used to calculate surface roughness, quantified by the R_a and R_z values in accordance with ISO 4287 [173].

4.2.5 Microcomputed tomography (μ CT)

Micro-strut gauge section morphology was accessed using μ CT. Scans were performed using a Scanco UCT40 desktop scanner (SCANCO Medical AG, Brüttisellen Switzerland) with an isotropic voxel size of 12 μ m, tube voltage of 70kVp and tube current of 114 μ A (Fig 4.05.a). Subsequently, boundary profiles of the μ CT scans were reconstructed in the MATLAB (Fig 4.05.b). Here, boundary data from the μ CT cross-sectional image stack was extracted using a thresholding technique. Following this, the gauge section of each micro-strut was isolated using a region of interest. These profiles were then aligned to the true z-orientation by using their centroidal axes as a reference. Morphological characteristics were then measured across each plane parallel to the z-axis. In this study, a number of key characteristics are classified representing deviations between as-designed and as-fabricated geometries. These include;

- **Aspect ratio:** SLM fabricated micro-struts are not perfectly cylindrical. Here, deviations from the as-designed cylindrical profile are captured using measurements of aspect ratio. This is measured for each cross-section using the major and minor axes of the best fitting ellipse.
- **Waviness:** Waviness describes a common case of feature misalignment where the axis of the strut deviates from the originally linear design. It is measured as the average deviation between the centroid of each cross-section and the centroidal axis of the entire strut.
- **Variable cross-section:** Variability along the strut extends to the equivalent radius of each cross-section. The wider the distribution, the less predictable is the outcome of the printing process.
- **Efficient cross-section:** Due to the presence of surface defects (particularly partially adhered powder), a significant volume of the strut is non-load bearing. The core load-bearing cross-section of the strut that is consistent along the gauge length can be described by the efficient cross-section. It is measured as the cross-

section with complete overlap of all preceding and succeeding cross-sections along the centroidal axis.

4.2.6 X-ray diffraction

Samples were scanned on a single crystal X-ray diffractometer (D8 Advance, Bruker, Billerica, MA) with Cu K_α radiation ($\lambda = 1.5418\text{\AA}$). Scans were performed over $20-90^\circ 2\theta$ at a step size of 0.02° , and dwell time of 2s per step. The diffracted X-rays were collected at each 2θ angle, and fitted to a model from existing diffraction data (International Centre for Diffraction Data) using the Rietveld method, in DIFFRAC.EVA software (Bruker, Billerica). Due to an unavoidable difference in sample height, the sample displacement error was corrected as below; which accounts for deviations from the geometry of diffraction [174].

$$\Delta 2\theta = \frac{114.59s \cos \theta}{R}$$

Eq. 9

Where; R is the radius of the diffractometer, s is the displacement from the centre of the diffraction circle, and θ is the diffraction angle.

4.2.7 Alpha lath measurements

For this analysis, the micro-strut samples were simplified to thin cylindrical struts, with the same height and gauge diameter as the dog-bone designs. This was required for localisation of the $\varnothing 300$, 500 and $700\mu\text{m}$ cross-sections.

Preparation of these cross-sections entailed a sequential grinding/polishing metallographic protocol. Samples were mounted along their longitudinal axis in conductive SEM resin using a TA automated mounting press, passed through a sequential grinding and polishing protocol (Grinding: P800, P600, P1500, P72500 for 1min/step at 30Mpa, 150rpm, complimentary rotation, and water lubricated. Polishing: $0.3\mu\text{m}$ Fume Silica (Labquip, Ireland) for 10min at 20Mpa, 150rpm, complementary rotation), and finally sonicated in an alcohol solution for 30 minutes. Following this, the polished samples were etched in accordance with ASTM E407 [175], using a mixture of HF and HNO_3 (Kroll's Etching Reagent, Labquip) for approximately 10s to reveal microstructural features.

Micrographs were then captured using a Zeiss ULTRA SEM microscope and SE2 detector. For quantification of microstructural features, segmentation of grains was first performed in ImageJ before conducting feature measurements in MIPAR (MIPAR, Columbus, OH) [176].

4.2.8 Hardness testing

Vickers microhardness testing was performed on polished cross-sections (perpendicular to the build direction) using a HV5 indenter on a Mitutoyo MVK-H1 hardness testing machine (Mitutoyo, Takatsu-ku, Kawasaki, Kanagawa), and in accordance with ASTM E384 [177].

4.2.9 Electron back scatter diffraction (EBSD)

EBSD scans were performed on polished samples at the Muyan R&D Centre, China. Analysis of the data was performed in Matlab using the MTEX toolbox.

4.2.10 Statistical analysis

Statistical analysis was performed using the software package GraphPad Prism (GraphPad, La Jolla, Ca). Statistical tests used to compare groups are indicated in figure legends. Significance was accepted at a level of $p < 0.05$. Results are expressed as mean $\pm$ standard deviation.

4.3 Results and discussion

4.3.1 Feature size dependent tensile properties

The mechanical properties of SLM fabricated micro-struts can be significantly different to the bulk material [15], [164]. In fact, the mechanical properties of micro-struts have been shown to exhibit feature size dependent behaviour with only relatively small changes in the strut diameter [15], [165]. In this work, we sought to characterize these effects between three different strut diameters ($\varnothing 300$, 500 and 700 μm ; Fig 4.01.c).

Here, the mechanical properties of the micro-strut samples are assessed in uniaxial tension. As quantified by the elastic modulus (Fig 4.01.d), the micro-strut samples exhibit a significantly lower stiffness than the material in its bulk form. These results coincide with recent studies in the literature for sub-micron struts [111], [165], [166], [178]. However, no significance can be observed for elastic modulus as a function of strut diameter (Fig 4.01.d).

On the contrary, the mechanical properties exhibit a dependence on feature size for both the yield strength, and failure strain. A drop in yield strength of 5.01% and 18.58% can be observed as strut diameter is decreased from $\varnothing 700\mu\text{m}$ to $\varnothing 500$ and $300\mu\text{m}$ respectfully. A number of published studies contradict our findings, suggesting an increase in yield strength as feature size is reduced. Generally, these studies have pointed towards refinements in micro-structure as a plausible explanation [15]. On the contrary, a number

of studies are in agreement with our findings, suggesting a decrease in yield strength as feature size is reduced, which was explained by the inheritance of topological and morphological defects [164]. Clearly, the yield strength of SLM fabricated titanium is affected by multiple factors. However, given the lack of systematic studies in the literature, it is difficult to attribute a proportional contribution for each effect.

The failure strain also exhibits a dependence on feature size. Here, a drop in failure strain by 43.52% and 65.08% can be observed as strut diameter is decreased from $\varnothing 700\mu\text{m}$, to $\varnothing 500$ and $300\mu\text{m}$ respectively. In this regard, the literature is more conclusive. In agreement with our findings, a decrease in failure strain is typically observed as feature size is reduced [15], [164], [165]. This is unsurprising, given both microstructural refinements, and the inheritance of topological and morphological defects, will have a negative effect.

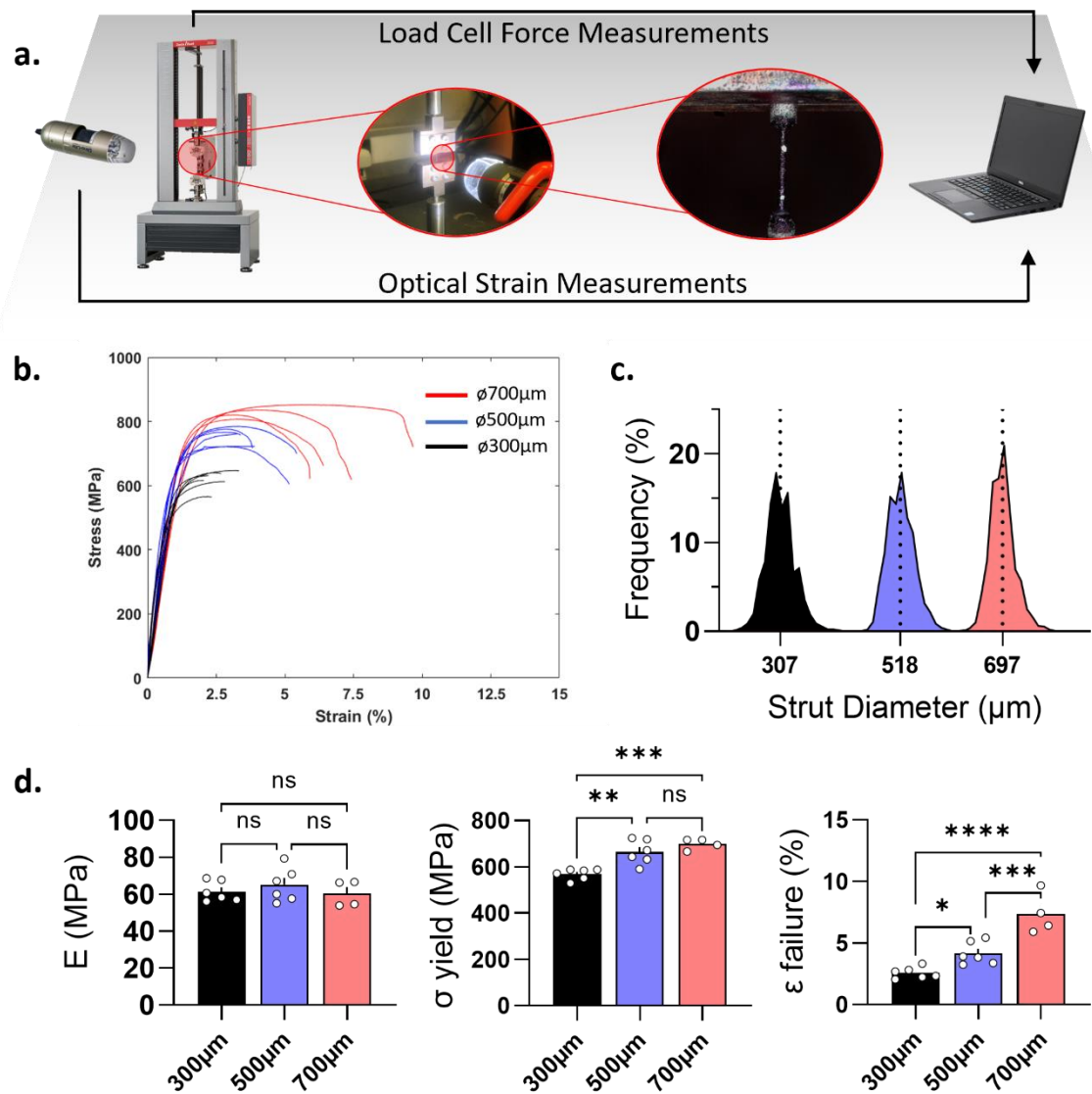


Figure 4.01. **Mechanical properties exhibit feature size dependent behaviour.** a) Micro-strut samples were then pulled to failure in uniaxial tension under displacement control, and b.) stress-strain curves were constructed. c.) In this study, the feature size was reduced from $\phi 700$ to $300\mu\text{m}$. d.) Over this range, a decrease in stiffness and failure strain can be observed. All error bars denote standard deviation, *, **, *** and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, one-way ANOVA).

SEM was next used to assess the mode of fracture (Fig 4.02). These results coincide with observations made during tensile testing (Fig 4.01) and point to a more brittle failure as strut diameter is decreased. For the larger $\phi 700$ and $500\mu\text{m}$ samples, a relatively ductile mode of failure can be observed, characterised by micro-void coalescence normal to the tensile axis (Region I), progressing into a region of shear failure normal to the axis of maximum principal stress (Region II) [179][165]. As strut diameter is decreased to $\phi 300\mu\text{m}$, a more brittle mode of fracture can be observed, characterised by a region of cleavage facets (Region A), progressing into a region of shearing dimples (B) [179], [180].

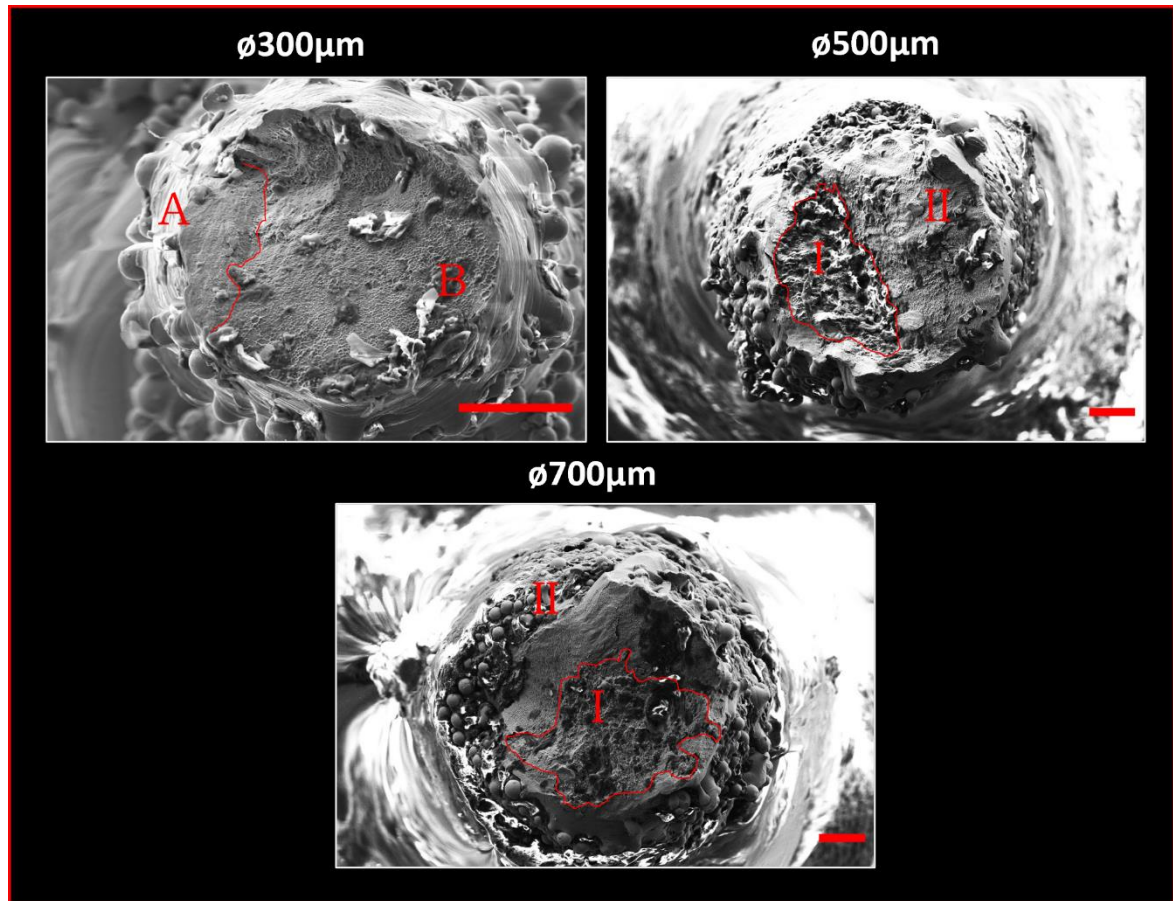


Figure 4.02. **Fracture surfaces indicate more brittle failure as feature size is reduced.** SEM showing representative fracture surfaces. In the larger $\phi 700\mu\text{m}$ group, a relatively ductile failure can be observed, progressing from a ductile region of micro-void coalescence (I), into a more brittle shearing mode (II). As feature size is reduced towards the smaller $\phi 300\mu\text{m}$ group, failure appears more brittle, progressing from a region of cleavage (A), into the shearing mode (B). Scale bars are equal to $100\mu\text{m}$ (red).

4.3.2 Feature size dependent fatigue properties

The mechanical properties of the micro-strut samples were also assessed in fatigue. Here, the fatigue properties were measured across each group (Fig 4.03.b and Fig 4.03.c). In order to investigate the mechanisms of failure, the fracture surfaces were also characterised alongside this work (Fig 4.04 and Fig 4.05). From SEM it is clear that the fractured surfaces are typical of fatigue fracture (Fig 4.04). River markings can be observed progressing from potential sites of crack initiation into the crack growth zone. As the crack progresses through the crack growth zone, striations can also be observed, representing the incremental growth of the crack under cyclic loading (Fig 4.04).[102], [156], [157], [158]

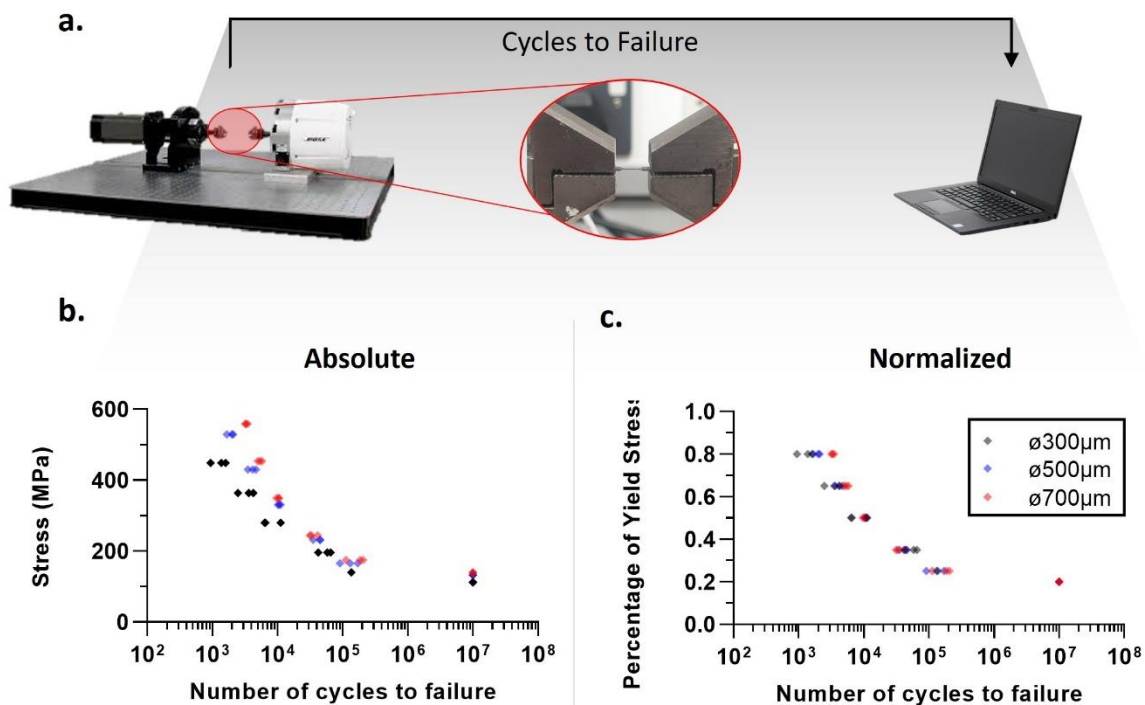


Figure 4.03. **Fatigue Properties exhibit feature size dependent behaviour.** a.) Micro-struts were tested in load controlled tension-tension fatigue at discrete percentages of the tensile yield strength. S-N curves were created by recording the number of cycles to failure at each loading increment. b.) Plotted against absolute stress, a feature size dependent number of cycles to failure can be observed at any given load. c) However, when stress is normalised to account for differences in tensile strength, this behaviour can only be observed under LCF loading.

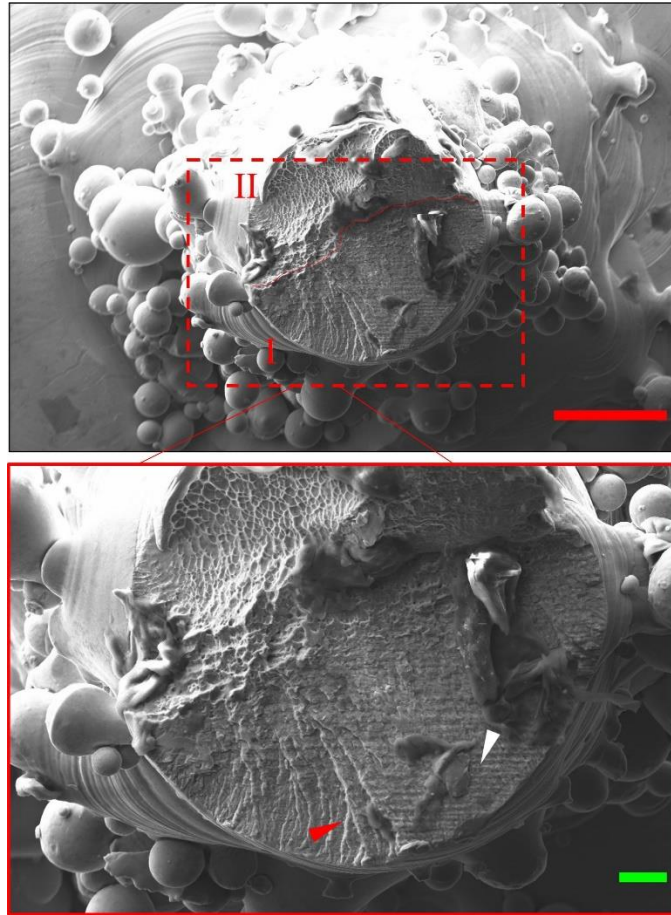


Figure 4.04. **Fracture surfaces are typical of fatigue fractures.** Fracture surfaces show typical markings of fatigue fracture. The crack growth and final fracture regions are indicated as Regions I and II respectively. River marking (red) can be observed progressing from the crack initiation zone into the crack growth zone, and striations (white), can be observed perpendicular to the crack growth in the crack growth zone. Scale bars are equal to 100µm (red) and 20µm (green).

As each sample group showed different yield strengths, the S-N curves were also normalised as percentages of the yield strength (Fig 4.03.c). This allowed us to capture the entire range of low cycle fatigue (LCF) to high cycle fatigue (HCF) [102], [156], [157], [158]. Here, a trend towards reduced resistance to LCF could be observed in the smaller diameter struts, while resistance to HCF was not affected by strut size (Fig 4.03.c).

LCF is characterised by the application of high stress, and a short number of cycles to failure. After nucleation, further crack growth is characterised by predominantly plastic deformation and resistance is derived from local material properties at the crack tip [101], [102]. At the other end of the S-N curve, HCF is characterised by the application of a relatively lower stress and a larger number of cycles to failure [101], [102]. In HCF crack growth, a much smaller plastic zone exists at the crack tip, and as a result, HCF is characterised by predominantly elastic behaviour. With the above in mind, resistance to

HCF is derived from predominately crack nucleation, whereas the effects of both crack nucleation and crack growth are typically notable under LCF.

At the far end of the S-N curve, run-out can be observed at 25% of yield strength across all groups. Although the fatigue properties of SLM fabricated titanium have not been extensively studied in small diameter struts, the literature for bulk material generally coincides with these results, suggesting runout in SLM fabricated titanium being much lower than traditionally fabricated material [178].

Before run-out, a similar number of cycles to failure can be observed under HCF loading conditions across the three strut diameters (Fig 4.03.c). As discussed, resistance to HCF is predominately derived from crack nucleation. From SEM, it is apparent that cracks generally nucleate from surface and near-surface defects across all groups (Fig 4.05). This is typical of SLM fabricated components, and a consequence of the inherently high surface roughness. Cracks are generally more likely to occur from such defects, as they typically experience high stress intensity factors (SIF) due to their surface free energy [24], [101], [110]. Beyond crack nucleation, a typically large crack growth zone (Region I), and small final fracture zone (Region II) can be observed.

Although not significant, a trend has emerged under LCF where a shorter number of cycles to failure can be observed as strut diameter is decreased (Fig 4.03.c). As discussed, resistance to LCF is derived from both crack nucleation and crack growth. Similar to HCF, crack nucleation can be generally observed in surface and near-surface defects (Fig 4.05). Consequently, the trend in LCF properties is most likely a consequence of resistance to crack growth. Typical of LCF, smaller crack growth zones are observed than that under HCF.

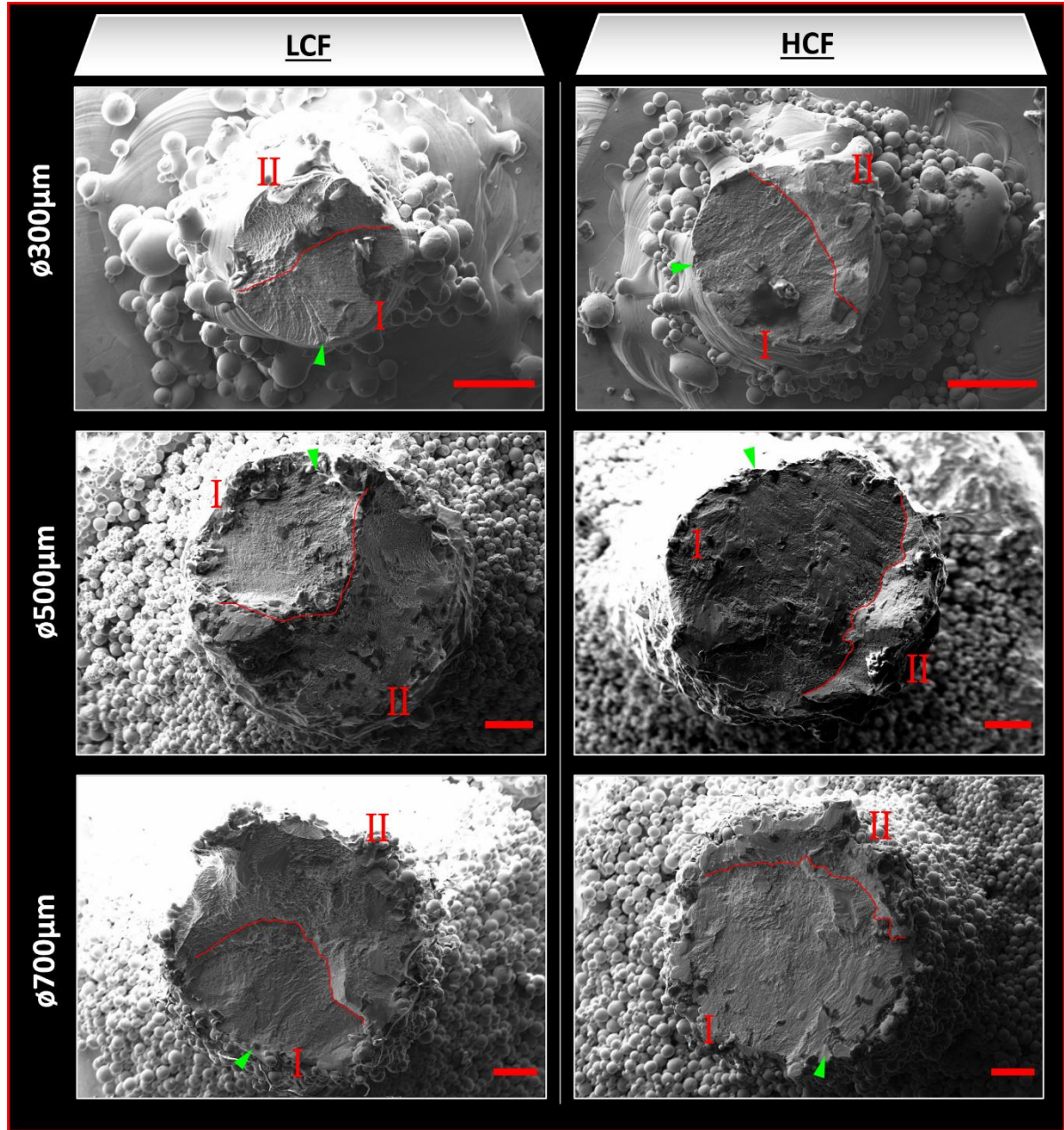


Figure 4.05. **Fracture Surfaces.** SEM showing representative LCF and HCF fracture surfaces for each strut diameter. Generally, crack initiation is located in surface and near-surface defects in both fatigue loading regimes. Potential sites for crack initiation are highlighted by a green arrow. The crack growth, and final fracture regions are indicated as Regions I and II respectively. Scale bars are equal to 100μm (red).

4.3.3 Topological defects inherited from the fabrication process

As crack nucleation was generally derived from surface and near-surface defects, we next sought to characterise the surface roughness (Fig 4.06). From SEM, it is apparent that the surface roughness of micro-strut samples is primarily derived from partially adhered powder. This is typical of SLM fabricated components, and largely unavoidable due to the physics of the melt pool, along with powder granule size and morphology [64], [71]. From WLI, quantification of R_a and R_z values indicate similar roughness across all groups, and

are in the typical range from SLM fabricated components. These results also coincide with the similar number of cycles to failure observed between groups under HCF loading conditions (Fig 4.06.c). This can be correlated to a similar degree of stress concentrations between samples, and a consequently similar energy needed to initiate a crack.

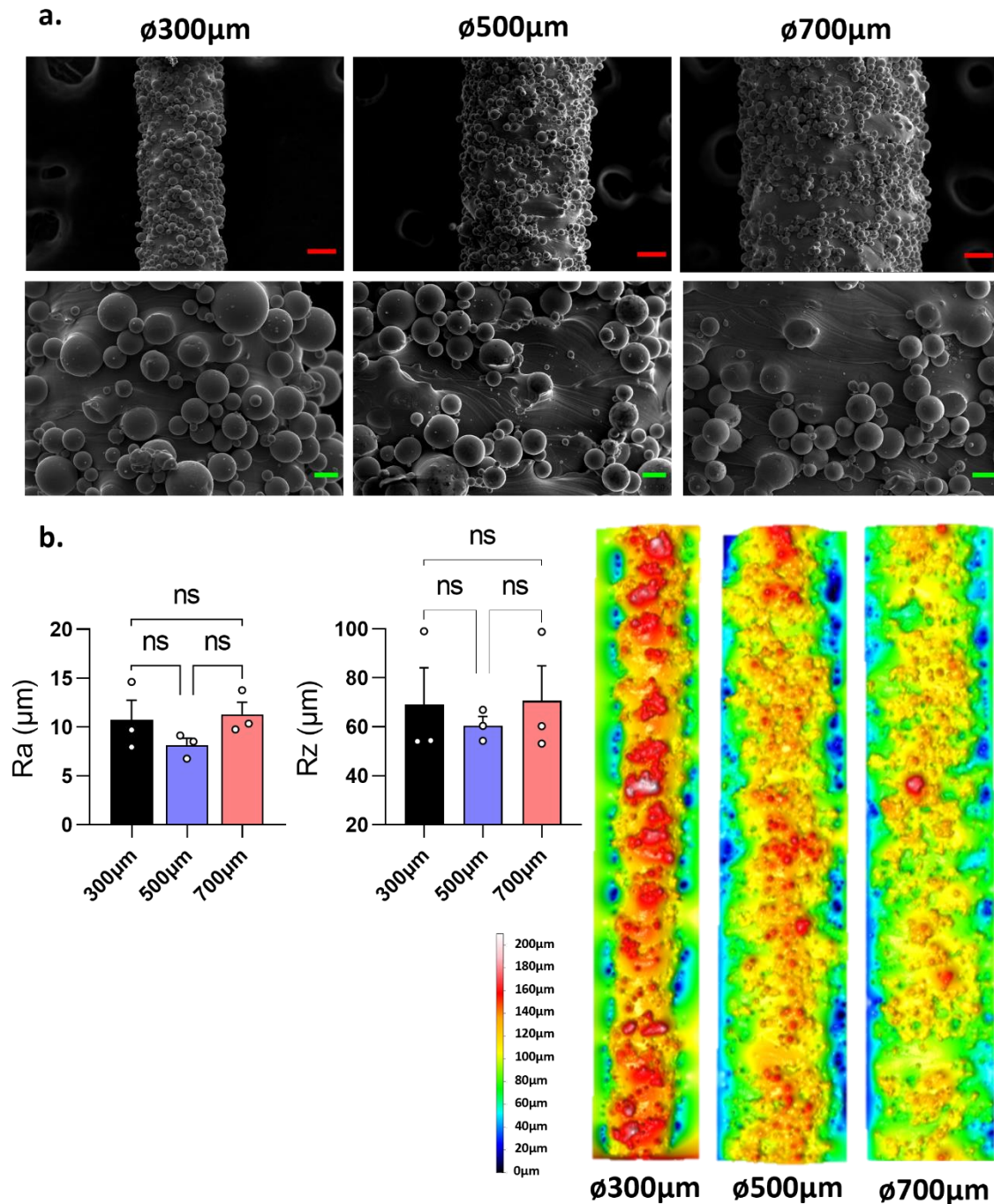


Figure 4.06. Surface roughness is characterised by partially adhered powder. a.) SEM, and b.) WLI reconstruction (right) clearly shows that the surface of all micro-strut groups is characterised by partially adhered powder inherited from the fabrication process. b.) WLI R_a and R_z measurements (left) indicate similar

roughness across all groups. Scale bars are equal to 100 μ m (red) and 20 μ m (green). All error bars denote standard deviation, ns, indicating no statistically significant differences, one-way ANOVA).

4.3.4 Morphological defects inherited from the fabrication process

In small diameter struts, surface defects account for a significant portion of the strut diameter, and can lead to a new class of irregularities described as morphological [71], [111], [166], [167], [168], [169], [170]. These defects act to impede structural and mechanical integrity beyond the effects of stress concentrations. This is a consequence of variations in strut cross-sections, which act to reduce the effective load-bearing capacity.

As described in section 2.7, morphological defects were captured using μ CT measurements of aspect ratio, strut waviness, and efficient cross-section (Fig 4.07.c). As expected, all groups exhibit deviations from the as-designed geometry, but a deterioration in strut morphology can be observed as strut diameter is decreased. This is reflected in a reduction in the aspect ratio and an increase in the waviness of the struts with reductions in diameter (Fig 4.07.c). This can be largely attributed to a higher portion of the strut diameter being accounted for by partially adhered powder.

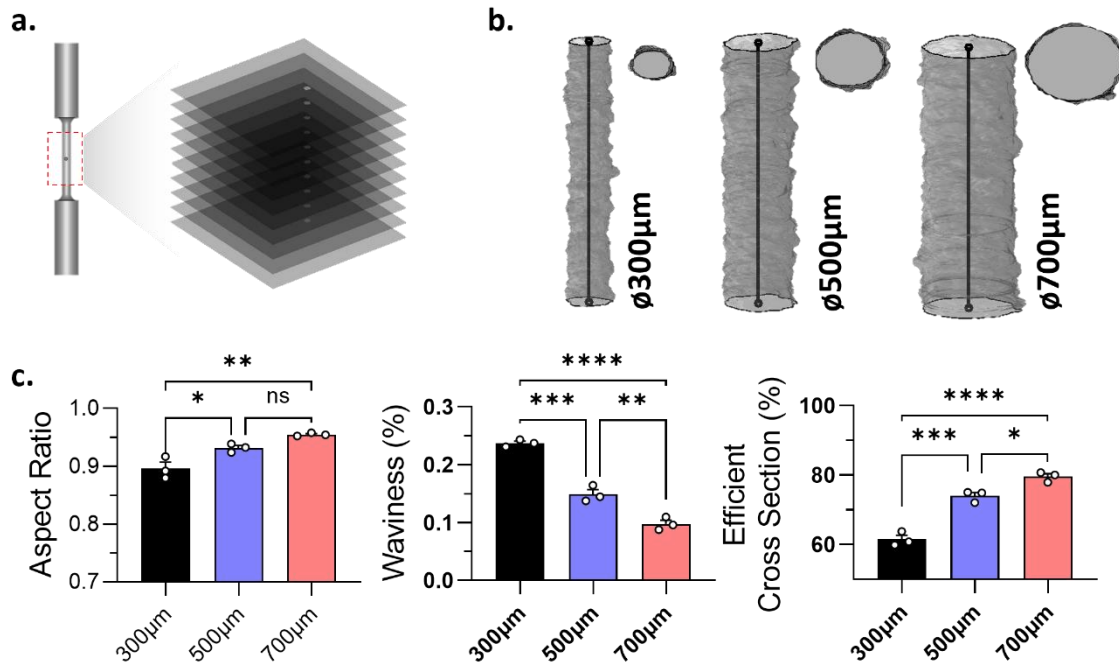


Figure 4.07. **Surface roughness drives feature size dependent morphological defects.** a.) Micro-strut surface profiles were reconstructed using μ CT. b.) These reconstructions clearly show the evolution of strut morphology with feature size. c.) This is quantified by measuring aspect ratio, waviness, and efficient cross-section. All error bars denote standard deviation, *, **, ***, and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, one-way ANOVA).

As strut morphology deteriorates, a reduction in the effective load bearing capacity can be observed. This can be quantified by the efficient cross-sectional area, which drops by 7.02% and 22.72% as strut diameter is decreased from $\varnothing 700\mu\text{m}$, to $\varnothing 500$ and $300\mu\text{m}$ respectively (Fig 4.06.c). These results coincide with the reduction in tensile yield strength (Fig 4.01.d) and HCF (Fig 4.03.c), which can be linked to a reduction in load-bearing capacity.

With the above in mind, the stress-strain curves for each group were normalised to the respective measurements of the efficient cross-section (Fig 4.08.a). This leads to a larger increase in stress for the smaller diameter struts, and consequently, the previously observed decrease in yield strength is no longer apparent (Fig 4.08.b). Similarly, a larger increase in elastic modulus can be observed in the smaller struts. This leads to a new trend, whereby an increase in stiffness can be observed as feature size is reduced. Previous studies have largely attributed this behaviour to differences in microstructure, driven by cooling rates [15], [76].

Normalisation to the respective measurements of efficient cross-section was also extended to fatigue (absolute), and subsequently by the new yield stress (normalised) (Fig 4.08.c). Previously, a reduction in the number of cycles to failure under LCF loading conditions could be observed as feature size was reduced. However, after normalising to the efficient cross-section, the number of cycles to failure is similar across all groups. Consequently, it is apparent that the previously observed feature size dependent behaviour was a result of higher stressing regimes in the smaller diameter struts.

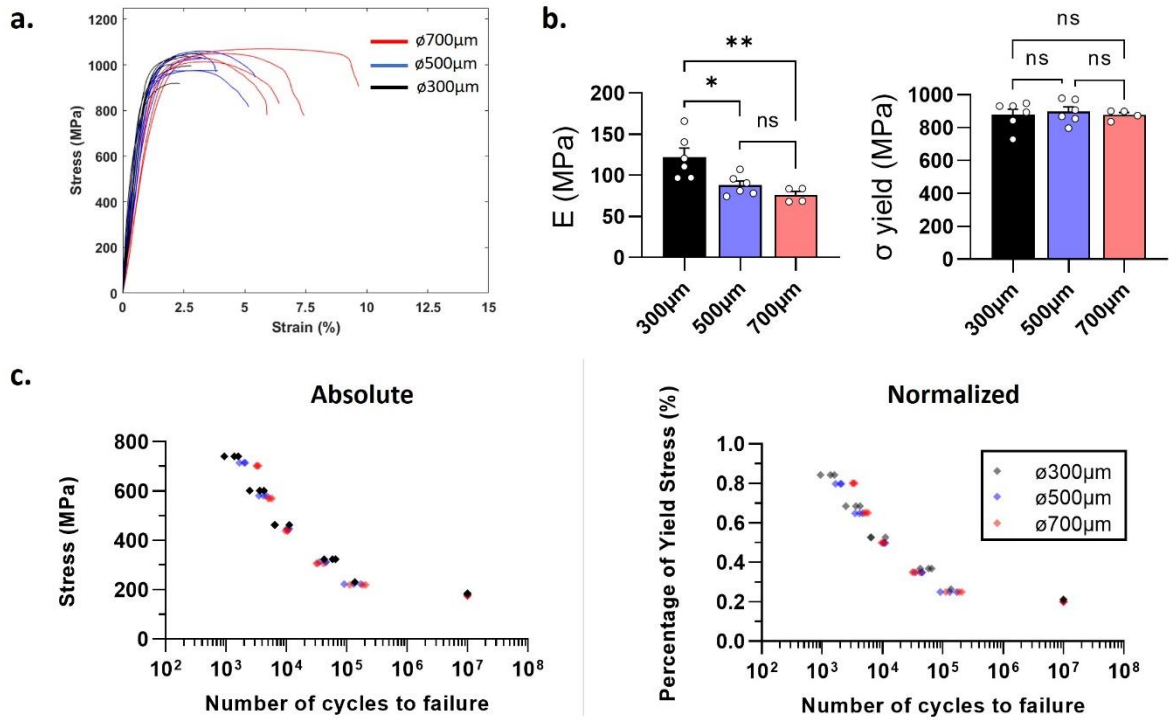


Figure 4.08. **Mechanical properties are affected by morphological defects.** Surface defects inherited from the fabrication process result in a reduction in the efficient cross-section responsible for load-bearing under tension. a.) After normalising the stress-strain curves to the respective measurements of efficient cross section, b.) the loss in yield strength as feature size is reduced is no longer apparent. Furthermore, an increase in stiffness can be observed as feature size is reduced. c.) Similarly, these effects are also apparent in fatigue. The S-N curve quantified by absolute stress (left) was normalised to the respective measurements of the efficient cross section. Subsequently, the normalised S-N curve (right) was plotted by normalising to the new yield stress. All error bars denote standard deviation, * and ** indicate statistically significant differences (* $p < 0.0332$ and ** $p < 0.0021$, one-way ANOVA).

4.3.5 Microstructure inherited from the fabrication process

Having normalised the tensile and fatigue properties to the measurements of efficient cross-section, feature size dependent behaviour can still be observed. This is apparent as an increase in stiffness (Fig 4.08.b) and a reduction in failure strain (Fig 4.01.d) as feature size is reduced.

Previously, similarly feature size dependent mechanical properties in micro-struts have been attributed to differences in microstructure [15]. Consequently, we next sought to characterise the microstructure of micro-strut samples (Fig 4.09). In this work, XRD indicated an entirely α microstructure (Fig 4.09.a). Due to rapid cooling rates inherent to SLM, the high temperature β phase of the titanium alloy transforms into predominantly α' martensite, with small amounts of remaining $\alpha + \beta$. However, the cooling rate in small feature size components is accelerated due to an increased surface to volume ratio, and

entirely α' martensite microstructures are commonly observed [15], [134]. Cooling rates below the martensite start temperature have also been shown to influence α' -lath thickness. As cooling rates are increased, α' -nucleation is promoted over propagation, resulting in finer α' -laths [15], [76], [134]. Consequently, α' -lath thickness has been commonly observed to reduce in smaller components [15], [76]. Coinciding with these studies, SEM indicated a reduction in α' -lath thickness as strut diameter was reduced (Fig 4.09.c & 4.09.d). A mean α' -lath thickness of 0.2011, 0.2326 and 0.3062 μm was observed in the $\varnothing 300$, 500 and 700 μm struts respectfully. An increase in microhardness could also be observed, and can be attributed to the higher density of grain boundaries (Fig 4.09.b).

As described by the Hall-Petch effect, finer α' -laths are commonly associated with higher strength; acting to disrupt dislocation movement and plastic flow [15], [134]. Despite this, no obvious trend could be observed in yield strength or ultimate tensile strength as a function of feature size (Fig 4.08.a & 4.08.b). Similarly, finer α' -laths are also associated with an increased resistance to fatigue; acting to arrest crack growth [116], [118], [181]. Despite this, no obvious trend in fatigue life can be observed in this work (Fig 4.08.c). However, an increase in residual stress could also be observed, evident as a shift in the XRD pattern (Fig 4.08.a). This is likely a consequence of an increased cooling rate, increasing the effective stress in the effective stress in the sample. Although the XRD patterns could be normalised to the respective sample heights, the patterns could not be normalised to the inherent differences in sample volume [174]. Consequently, and standing as a limitation of this work, the residual stress could not be measured quantitatively.

In addition to these effects, smaller grains are often associated with a reduction in the strain to failure [15], [76]. A lower strain to failure was observed in the smaller diameter struts (Fig 4.01.d). This can be correlated with a reduced possible dislocation slip length in smaller grain microstructures, consequently impeding plastic flow [134].

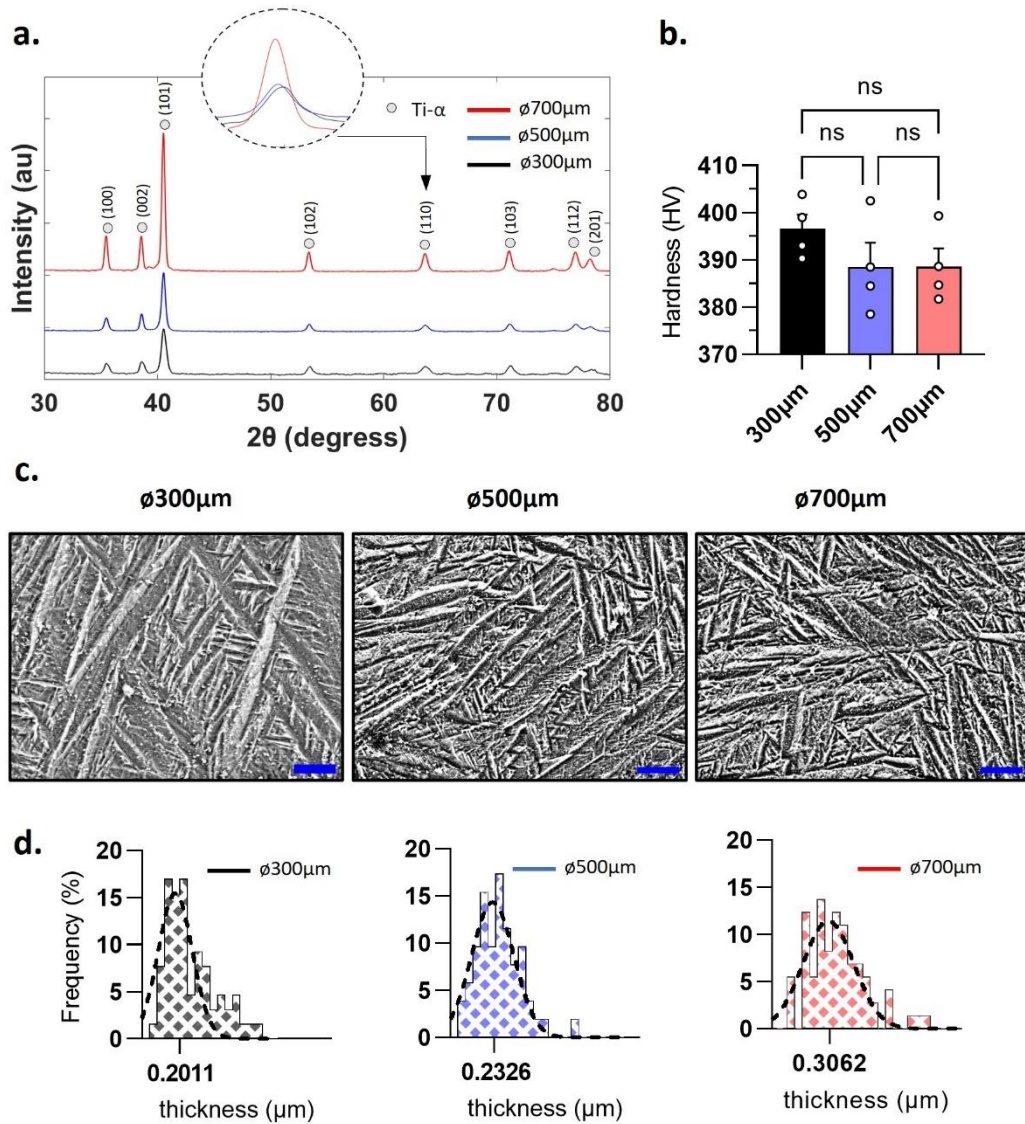


Figure 4.09. **α -lath thickness is influenced by feature size.** a.) Micro-strut samples are characterised by a HCP α' martensite microstructure. b.) Micro-hardness was measured using the Vickers method. c.) The α -lath thickness was imaged and, d.) measured using SEM, and exhibits a synonymous relationship with feature size. Scale bars are equal to 10 μ m (red). All error bars denote standard deviation, ns, indicate no statistically significant differences, one-way ANOVA).

It is well established that the HCP α -phase exhibits mechanical anisotropy as a consequence of crystallographic orientation [128], [129]. In SLM, the α' phase generally exhibits an inherently weak texture [126], [172]. This can be attributed to the high number of variants that precipitate within each columnar β grain. However, from EBSD, it is apparent that the micro-struts exhibit a relative increase in texture as feature size is reduced (texture index; ø300 μ m=14.55, ø500 μ m=9.78 and ø700 μ m=4.55). This is most apparent in the smaller ø300 μ m strut, which indicates a relatively higher texture towards $\langle 0001 \rangle$. Coinciding with these results, an increase in texture from SLM processing has been previously attributed to higher thermal gradients. However, in Ti-6Al-4V, the

evolution of texture is strongly dependent on the prior- β phase, as well as the final α -phase. Consequently, reconstruction of the prior- β grains using larger EBSD scan areas may have provided a more thorough explanation for the development of texture within each group.

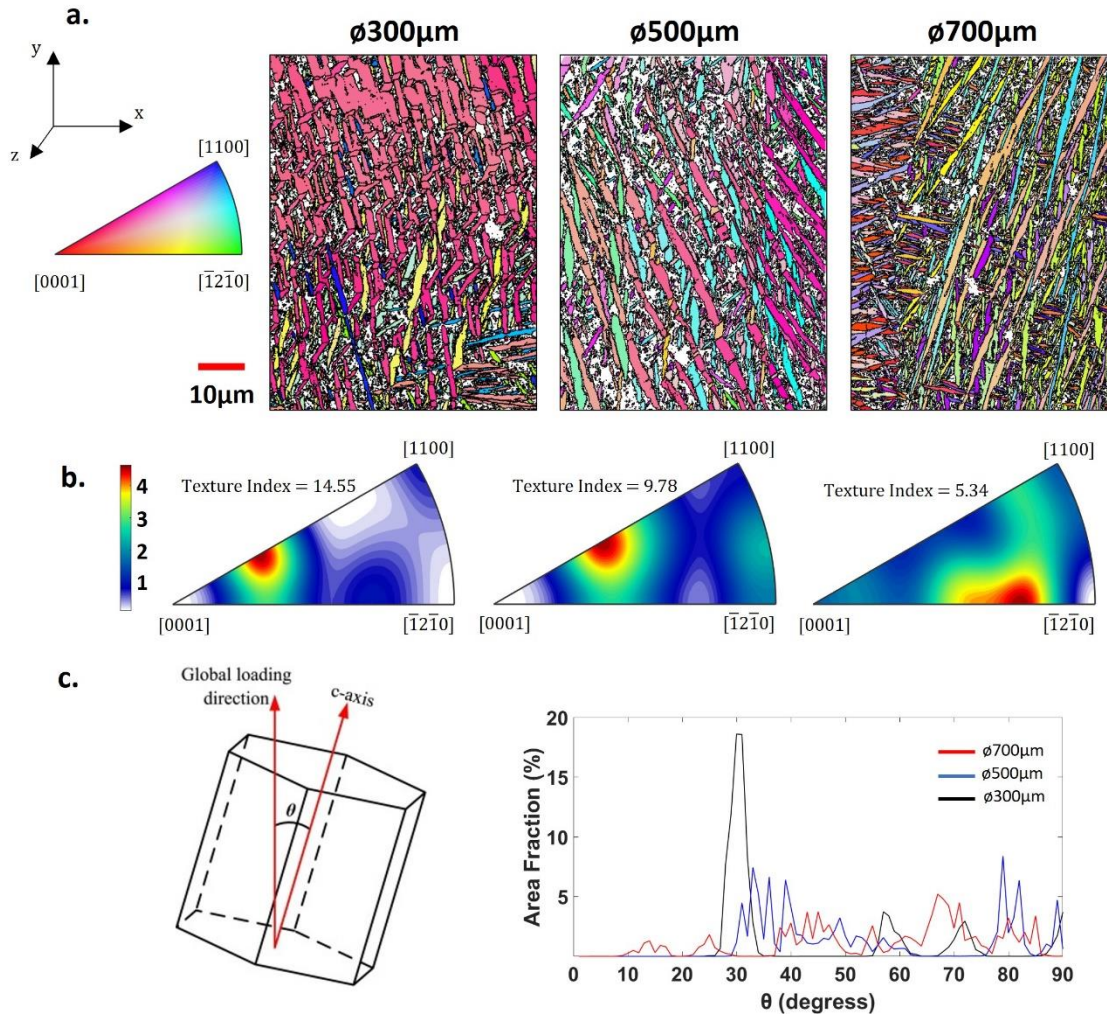


Figure 4.10. **Texture is influenced by feature size.** From EBSD a.) inverse pole, and b.) pole figures, an increase in crystallographic texture towards $\langle 0001 \rangle$ can be observed relative to the y-axis (tensile/build direction), as feature size is reduced. c.) As a result, a high area fraction of the $\phi 300 \mu\text{m}$ strut is characterised by low angles between the c-axes and global loading direction. Scale bars are equal to $10 \mu\text{m}$ (red).

We next sought to interpret the effects of crystallographic texture on mechanical properties. In HCP materials, the c-axis is often associated with higher stiffness due to the strong atomic bonding along this direction. This can lead to an increase in stiffness for grains with their c-axes aligned close to the global loading direction [128], [129]. Due to the strong texture towards $\langle 0001 \rangle$, a high area fraction of the $\phi 300 \mu\text{m}$ strut is characterised by low angles between the c-axes and global loading direction (Fig 4.10.c). These results may explain the significantly higher effective modulus value observed in the $\phi 300 \mu\text{m}$ struts compared to the larger $\phi 500$ and $700 \mu\text{m}$ struts (Fig 4.08.b).

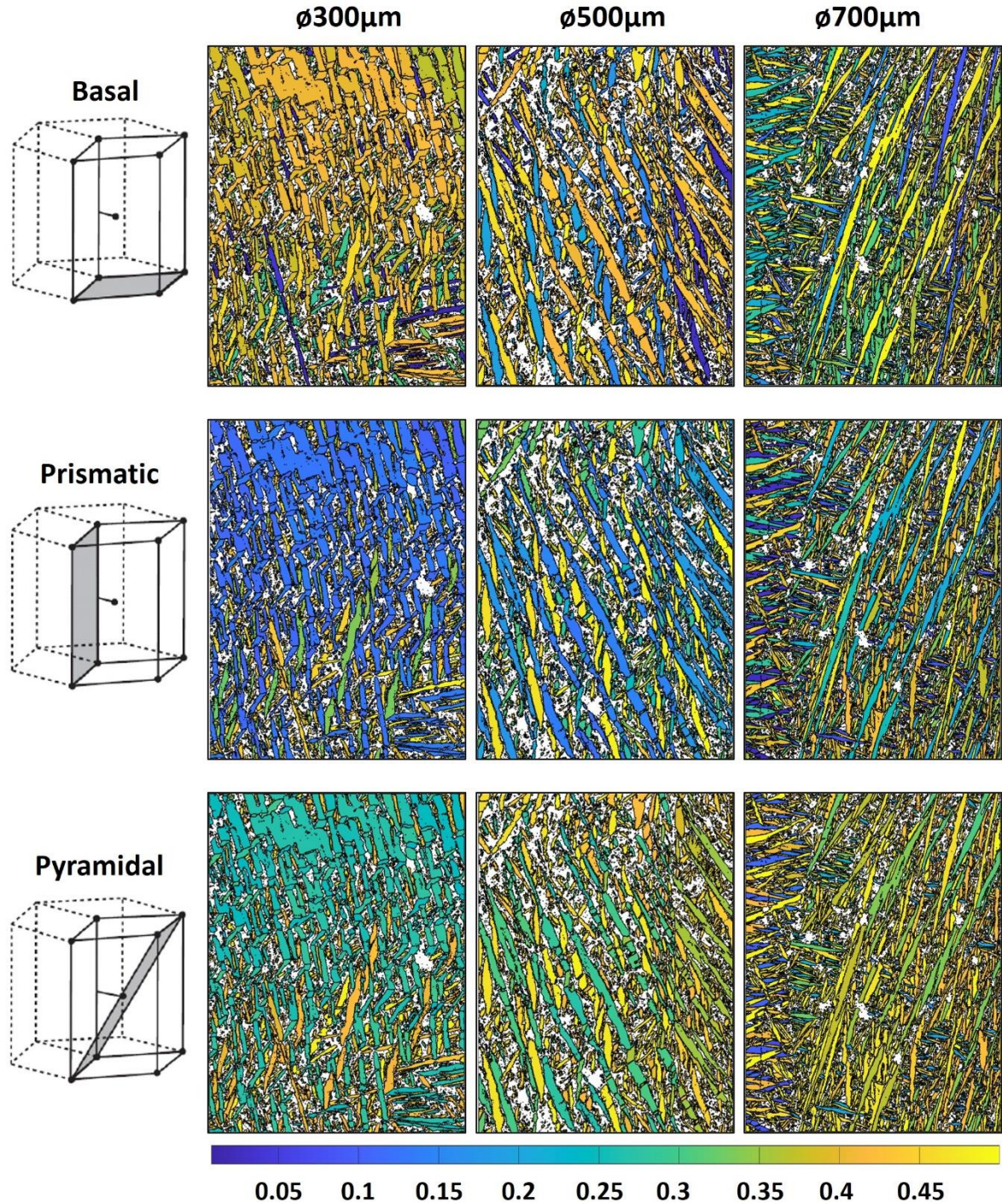


Figure 4.11. **Schmid Factors.** The Schmid factor governs how external applied stress is translated into resolved shear stress on each slip plane. The Schmid factor for Basal (top), Prismatic (middle) and Pyramidal (bottom) slip systems is plotted on each grain.

Beyond elasticity, both planar slip and twinning mechanisms contribute to the plasticity of materials. However, twinning is considerably suppressed in Ti-6Al-4V as a consequence of the high aluminium content [128], [129]. Consequently, planar slip is commonly considered as the primary deformation mechanism [128], [129], [130]. In HCP materials, slip is accommodated on basal, prismatic and pyramidal planes [128], [129]. The relative

strength of each slip plane contributes to plastic anisotropy. Generally, the basal and prismatic slip systems are more easily activated than pyramidal slip [129]. However, activation of a particular slip system is also dependent on crystallographic orientation to the applied load. The Schmid factor describes the resolved shear stress on each slip system due to the applied load [128], [129]. In this work, the $\varnothing 300\mu\text{m}$ strut exhibits a high Schmid factor for basal slip (Fig 4.11). Here, a Schmid factor above 0.35 was observed across 83% of the area within the $\varnothing 300\mu\text{m}$ strut, compared to 68%, and 35% in the $\varnothing 500$ and $700\mu\text{m}$ struts, respectively. Consequently, a lower applied stress is required to reach the critical resolved shear stress for basal slip. Furthermore, since basal slip is arguably the easiest slip system to activate in the HCP Ti-6Al-4V α phase, a lower applied stress would be required for plasticity, possibly negating the expected increase in strength from the finer α' -laths (Fig 4.09.d).

Finally, a decrease in the strain to failure was also observed as feature size was reduced (Fig 4.01.d). When combined with the cleavage failure mechanisms observed in the smaller $\varnothing 300\mu\text{m}$ struts, this suggests a more brittle response with little plastic deformation (Fig 4.02). Cleavage failure is associated with the propagation of cracks along specific crystallographic planes [180]. Consequently, cleavage failure is often associated with an increase in crystallographic texture, which coincides with our findings [182].

4.4 Conclusion

In this study, the mechanical properties of SLM fabricated Ti-6Al-4V micro-struts were investigated as a function of strut diameter. Feature size dependent mechanical properties could be observed under both tensile and fatigue loading, and related to multiple characteristics inherited from the fabrication process. By studying these characteristics systematically, their individual contribution towards mechanisms of deformation and failure could be established.

We concluded that surface defects inherited from the fabrication process such as partially adhered powder are non-load bearing, yet represent a significant percentage of the total material volume. Consequently, measurements of the core load-bearing cross-section is overestimated, and result in an underestimation of stress. These effects are increasingly notable as strut diameter is reduced, and appear as an increase in stiffness and a reduced resistance to plasticity under tensile and fatigue loading.

After the normalisation of stress to measurements of the effective load-bearing area, the effects of microstructural characteristics became more apparent. This could be observed as an increase in stiffness in small diameter struts, and credited to an increase in texture

towards $\langle 0001 \rangle$, resulting in a high area fraction characterised by low angles between the relatively stiff c-axes and the global loading direction.

The effects of microstructural characteristics were also apparent in the mechanism of failure. A reduced failure strain along with a more cleavage like fracture indicated an increasingly brittle failure as feature size was reduced. This could be correlated to a high texture towards $\langle 0001 \rangle$, promoting the propagation of cracks along the low energy basal slip plane, with limited plastic deformation.

Chapter 5: Morphological induced improvements in the bulk mechanical properties of chemically etched additively manufactured Ti-6Al-4V micro-strut lattices

This chapter has been published in the journal of ‘Additive Manufacturing’, under the title ‘Morphological induced improvements in the bulk mechanical properties of chemically etched additively manufactured Ti-6Al-4V micro-struts’, and is co-authored by Conor O’Keeffe, David Taylor, Caitriona Lally and Daniel J Kelly.

D, T provided expert opinion on fracture mechanisms. C, L and D.J, K supervised this work.

Abstract

Powder Bed Fusion (PBF) additive manufacturing techniques have enabled the fabrication of geometrically complex porous metallic lattice structures. Despite the many advantages of this approach, surface and near surface defects inherited from the fabrication process act to limit their structural and mechanical integrity. Consequently, surface cleaning techniques such as chemical etching have been increasingly adopted post process. Although the benefits of this technique have been captured across a range of lattice structures, the existing body of work is typically a characterisation of the engineering mechanical properties of lattices, rather than the bulk mechanical properties of the material. From a design perspective, the characterisation of such properties is fundamental to the prediction of mechanical performance and failure mechanisms.

In this study, standardised micro-strut dog-bone geometries were adopted as a means of isolating geometrical variations between lattice designs; allowing us to study the bulk mechanical properties of the material. Incremental etching was conducted and changes to both the surface and morphological properties of the micro-struts was characterised. Improvements in these factors was associated with a corresponding increase in mechanical properties. Both strength and stiffness increased following the removal of process inherited surface defects, which can be linked to the removal of non load bearing material. Failure strain and fatigue resistance also improved following surface etching, although similar fracture surfaces were observed in both groups. Together these findings demonstrate the benefits of chemical etching for improving the mechanical properties of additively manufactured Ti-6Al-4V lattice structures.

5.1 Introduction

Powder bed fusion (PBF) additive manufacturing techniques have enabled the fabrication of geometrically complex porous metallic lattice structures, and as such have been widely

adopted for orthopaedic implants and bone-tissue engineering applications [11], [43]. When applied to biomedical implants, these lattices offer advantages over traditional non-porous implants by allowing tissue ingrowth and more closely recapitulating the stiffness gradients of the native tissue [8], [9].

Among PBF technologies, selective laser melting (SLM) is comparatively more suited to small feature resolution [10], [11], [183], [184]. This has lent itself well to the fabrication of lattice structures, where the average strut size is in the range of a few hundred microns [11]. Despite the near-net shape capabilities of SLM, variations between the as-designed and as-fabricated geometries remain an issue. This is a result of near-surface geometrical defects inherited through the SLM process [64], [71], [72], [145], [159]. Unavoidably, powder granule size and morphology along with the physics of the melt pool result in partially adhered powder on external surfaces [64]. In instances of inclined surfaces, the stair casing effect may also occur [159]. Stair casing occurs when any curved surface is discretised into a number of laminar slices. Overhanging sections on the approximated bottom surface are partially built on loose powder, which by thermal diffusion sticks to the strut surface. It is well understood that the presence of these defects are detrimental to mechanical properties. This is particularly detrimental in small diameter strut lattices, as they experience these defects in high frequency and severity due to an increased surface to volume ratio [145]. In general, the fatigue resistance of SLM manufactured components is controlled by these near-surface defects as they typically experience high stress intensity factors (SIF) due to their surface free energy [23], [24], [101], [109], [110]. In tension they can modify the development of local plasticity, resulting in reduced ductility.

In small diameter struts, surface defects can also lead to a class of irregularities described as morphological, which act to further impede structural and mechanical integrity [71], [72], [167], [168], [169], [170]. For example, deviations between the as-designed and as-fabricated geometry may occur, including strut oversizing, and transition to a more elliptical-like profile [71]. Consequently, variable lattice properties can be expected, extending to, for example, stiffness and strength [167]-[168]. Large variations in strut cross-sections may also arise, which negatively impact mechanical performance by reducing the effective load bearing capacity [72]. Often described as strut waviness, misalignment of the centroid of each cross-section from the centroidal axis of the strut can also occur, similarly acting to degrade effective load bearing capacity [72], [169], [170].

In light of the aforementioned factors, SLM fabricated biomedical implants usually require a further surface cleaning post-processing step [185], [186], [187]. For non-porous implants, numerous surface treatments are available [188], [189]. However, the majority of these approaches rely on a line of sight with the surface and are not suitable for internal

features. Chemical etching has proven a suitable alternative in such instances [168], [190], [191], [192]. Applied to titanium alloys, chemical etching with a mixture of hydrofluoric acid (HF) and nitric acid (HNO_3) is commonly employed [190], [191], [192]. In this combination, HF acts as the effective etching reagent while HNO_3 acts to reduce hydrogen absorption and subsequently embrittlement [193], [194].

The benefits of chemical etching of lattice structures have been identified in the literature [190], [191], [192]. By removal of near-surface defects, the percentage of load bearing material is increased and the number of critical sites for failure is reduced. These benefits strongly depend on the geometrical aspects of the lattice, however repeatably result in a desirable increase in the stiffness-to-density ratio [167], [192], [195]. Although these improvements have been shown across a wide range of lattice structures, the existing body of work is a characterisation of the engineering mechanical properties of lattices, and not the bulk mechanical properties of the material. From a design perspective, material properties are considered the basic building blocks of any structure [71], [196], [197], [198], [199]. Their characterisation is fundamental to the prediction of mechanical performance and failure mechanisms.

Recently, a number of studies have attempted to characterise these properties in as-built lattice structures [71], [72], [91], [145], [200], [201]. These studies have isolated geometrical aspects between lattice designs by using adaptations of ISO and ASTM dog-bone geometries, printed on the same scale as the micro-strut building blocks of the lattice. From this work, it is becoming apparent that the mechanical properties of micro-struts can be significantly different to the bulk material. These effects are understood to derive as a result of the compromising effect of process inherited factors from SLM manufacturing. As a result of the small feature size, these factors are inherited by the strut disproportionately, and consequently have a more detrimental effect on mechanical properties [71], [72], [145]. Among these compromising factors, are the aforementioned near-surface and morphological defects. It is therefore the objective of this study to use chemical etching to minimise these defects, and ultimately characterise the potential improvement in material properties. To the best of our knowledge, the material properties of chemically etched titanium micro-struts have not been thoroughly characterised; this represents a significant gap in the literature which impacts our capacity to design and manufacture lattice structures.

In this study, we investigate chemical etching of SLM fabricated Ti-6Al-4V on 1.) a standardised micro-strut geometry and 2.) a lattice geometry, using a mixture of HF and HNO_3 . This extends to the characterisation of the potential surface and morphological improvements and any subsequent changes in mechanical properties.

5.2 Methods

5.2.1 Design & manufacturing

Micro-strut and lattice samples were designed using the computer-aided-design (CAD) software Autodesk Inventor and Autodesk Netfab (Autodesk, San Francisco, Ca). Micro-strut samples were designed as cylindrical dog-bone samples of various guage diameters ($\varnothing 500$ and $700\mu\text{m}$) and dimensional ratios proportional to ASTM E8. Lattice samples was designed as a 10mm^3 structure, homogenously infilled with the 2mm^3 tetra unit cell. Two different variations of this lattice were designed, with the intention of having an as-built and chemically etched group with comparable strut diameters. Therefore, struts in the as-built group were designed as $\varnothing 500\mu\text{m}$, whereas struts in the etched group were designed slightly thicker as $\varnothing 550\mu\text{m}$.

All samples were built using a Realiser SLM 50 manufacturing system (spot size = $160\mu\text{m}$) (DMG MORI, Bielefeld, Germany) and Ti6Al4V, Grade 23 (particle size = $10\text{-}45\mu\text{m}$) powder under an argon controlled atmosphere ($\text{o}_2 < 0.2\%$). The CAD geometry was processed in $0.25\mu\text{m}$ slices, using a contour-and-hatch (C&H) laser scanning strategy. C&H printing parameters were adopted from Chapter 3.

After printing, samples were removed from the build plate using electrical discharge machining (EDM) and sonicated in an isopropyl alcohol solution for 30 minutes to remove loose powder.

5.2.2 Chemical etching

Samples were chemically etched using a mixture of HF and HNO_3 (Kroll's Etching Reagent, Labquip). Micro-strut and lattice samples were etched by placing them into baths of the etching solution filled to a ratio of 50ml per 10g. The micro-strut samples were etched to 12, 30 and 105 minute time points, while the lattice samples were etched to the 12 minute time point only.

After etching, samples were sonicated in an alcohol solution for 30 minutes, in deionised water for 30 minutes, and left to dry at room temperature.

5.2.3 Brightfield microscopy

Micro-strut guage diameters were measured at each etching time point using brightfield microscopy. Micrographs of the guage sections were acquired at $\times 2.5$ magnification on an Olympus SZX7 stereomicroscope (Olympus, Tokyo), and strut diameter was measured in the programming software MATLAB (MathWorks, Cambridge, UK) using a thresholding

technique to extract a boundary profile of the strut, and subsequently measuring the diameter across a number of points perpendicular the centroidal axis.

5.2.4 Surface roughness measurements

Surface roughness was characterised at each etching time-point for the micro-strut samples using a Filmetrics Profilim 3D white light interferometry (WLI) (KLA Instruments, Milpitas, Ca). Measurements were taken along the z-axis of the micro-strut gauge sections at x50 magnification, and used to calculate surface roughness, quantified by the R_a and R_z values in accordance with ISO 4287 [159].

5.2.5 Microcomputed tomography (μ CT)

Modifications in micro-strut and lattice morphology after chemical etching was accessed using μ CT. 0 and 12 minute time-points were scanned using a Scanco UCT40 desktop scanner (SCANCO Medical AG, *Brüttisellen Switzerland*) with an isotropic voxel size of 12 μ m, tube voltage of 70kVp and tube current of 114 μ A. 3D profiles of the scans were reconstructed in the MATLAB using a thresholding technique to extract boundary data from the μ CT cross-section image stack. For analysis of this data, a region of interest (ROI) was used to extract simple profiles of the gauge sections from the micro-strut samples, and individual struts from the lattice samples. Centroidal axes of these profiles were then used as a reference in order to align the strut in the true z-orientation. Morphological characteristics were then measured across each plane parallel to the z-axis. In this study, a number of key characteristics are classified, capturing the mismatch between as-designed and as-fabricated geometries. As discussed in Chapter 4, these extend to aspect ratio, waviness, variable cross-section, and efficient cross-section.

5.2.6 Mechanical testing

Tensile tests were carried out on micro-strut samples. Tests were performed under displacement control at a strain rate of 0.5%/s until failure on a Zwick universal testing machine (Zwick ZO05, Zwick GmbH & Co. Ulm, Germany) equipped with a 200N load cell. Cross-sectional areas used to calculate stress were assessed using the aforementioned brightfield microscopy approach. Strain was measured optically using a video extensometer approach, further detailed in Chapter 2. Elastic modulus (E), Yield Strength (σ_{yield}) and Failure Strain ($\epsilon_{failure}$) were calculated for each sample from the stress-strain data in accordance with ASTM E8 [202].

Mechanical testing of the micro-strut samples was extended to fatigue properties. Tests were performed on TA Instruments test bench system (Waters, Milford, MA) equipped with a 200N load cell. Samples were subjected to tension-tension (R=0.1) cyclic loading at

50Hz under load control at 80, 65, 50, 35, 25 and 20% of the yield strength. S-N curves were constructed by noting the number of cycles to failure at each load level, or in the absence of failure by runout ($N = 10^7$ cycles).

Compression tests were also carried out on lattice samples. Tests were performed under displacement control at a strain rate of 0.5%/s on an Instron 8801 testing system (Instron, Northwood, MA). Force was measured on a 100kN load cell and a callipers was used to measure the cross-sectional area for stress calculations. Strain was measured via crosshead displacement. Toe regions were removed from stress-strain curves in accordance with ISO 13314 [203], and E , σ_{yield} , and the Ultimate Compressive Strength (UCS) were calculated similarly to tensile testing.

5.2.7 Scanning electron microscopy (SEM)

Characterisation of micro-strut and lattice surface morphologies were assessed at each etching time-point using SEM. Images were taken using a Zeiss ULTRA microscope (Carl-Zeiss-Stiftung, Heidenheim, Germany) and SE2 detector with 60 μ m aperture, 15kV excitation voltage and 12mm working distance. Tensile and fatigue fracture surfaces were also assessed for fractography characterisation under the same conditions.

5.2.8 Statistical Analysis

Statistical analysis was performed using the software package GraphPad Prism (GraphPad, La Jolla, Ca). Statistical tests used to compare groups are indicated in figure legends. Significance was accepted at a level of $p < 0.05$. Results are expressed as mean $\pm$ standard deviation.

5.3 Results and discussion

5.3.1 Chemical etched micro-struts

A mixture of HF and HNO_3 was adopted for chemically etching Ti6Al4V. HF readily reacts with Ti to form Ti hexafluoride complexes and hydrogen gas resulting in material removal, and in the case of lattice structures a reduction in strut size [193], [194], [204]. However, the rate of this reaction is affected by the surface area available and variable results have been reported in the literature as a consequence of lattice topology [190], [191], [192], [195]. It is therefore necessary to characterise the etching process for each specific design.

Chemical etching reduced strut diameter, with larger reductions observed for longer etching times (Fig 5.01.a & 5.01.b). Both the $\varnothing 500\mu$ m and $\varnothing 700\mu$ m samples exhibit large initial reductions in strut diameter following 12 minutes of etching. This is followed by a gradual tapering off at subsequent time points. There are two possible explanations for

this trend. As the reaction progresses the available etching reagent begins to deplete [193], [194]. However, the majority of studies have kept the volume of the reagent relatively high and not considered its depletion [190], [191], [192], [195], [205]. Rather, these studies have linked such temporal trends to changes in the surface area during the etching process [190], [191], [192], [194], [195], [205]. In the early phases of the etching process, the reagent is in contact with the rough as-built strut surface. This possesses a relatively large total surface area and therefore is associated with an increased local density of the reagent per unit volume of material [192], [195]. This leads to higher rates of material removal. In this work, imaging of the micro-strut surfaces shows a similar trend (Fig 5.01.c). Both the 500 and 700 μ m samples exhibit the highest density of defects in their as-built form. Additionally, the most apparent modification in surface topology occurs between the 0 and 12 minute time-points. Following this, etching becomes more difficult. At subsequent time-points, a significant proportion of surface defects have been removed, and the reagent is in contact with the much smoother bulk surface. This represents a decrease in the total surface and drives a subsequent decrease in the local density of the reagent [192], [195]. Consequently, continued etching of the remaining bulk surface continues, but becomes less effective. This is apparent in Fig 5.01.c where only a small improvement in surface topology can be observed after the 12 minute time-point.

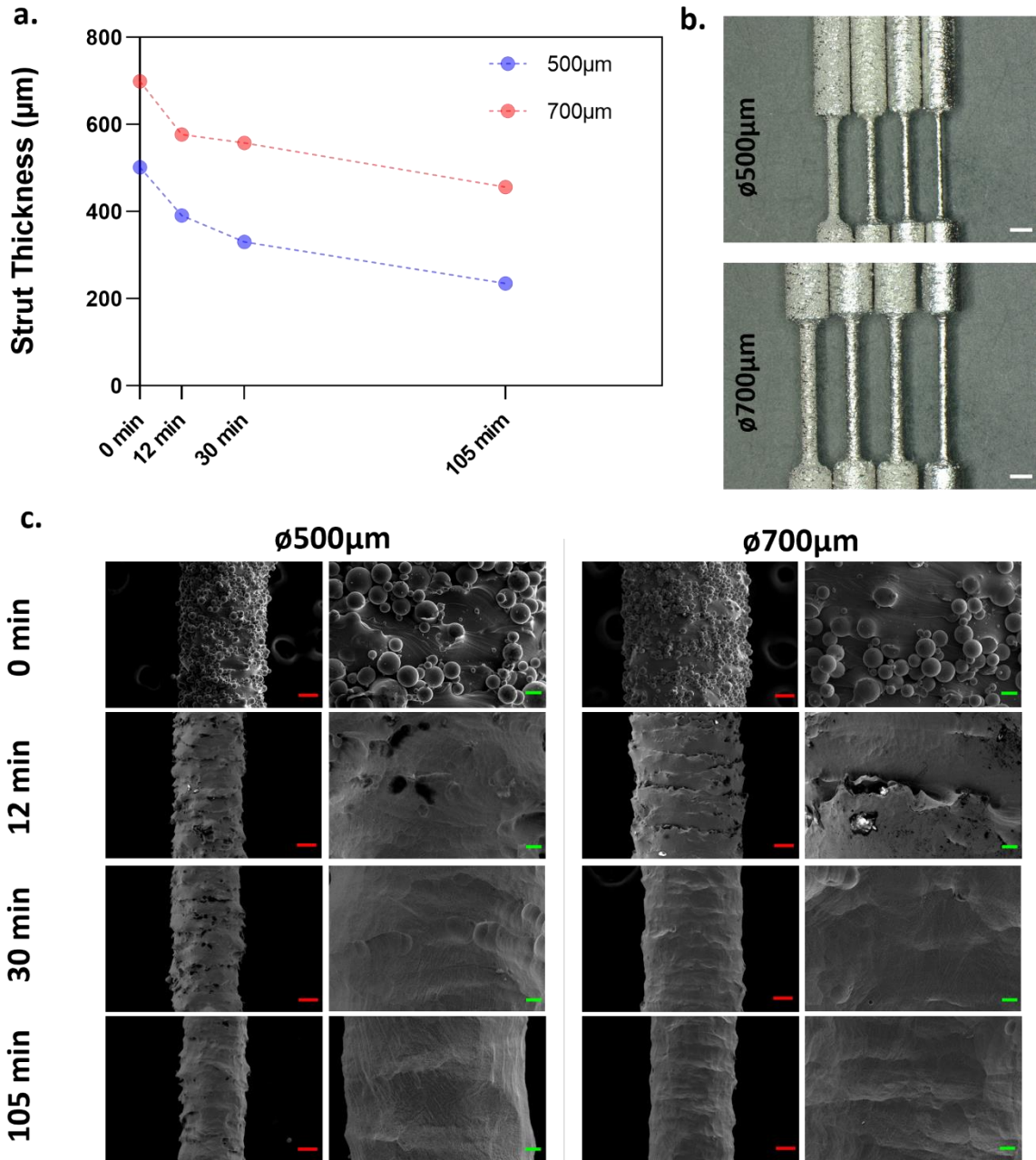


Figure 5.01. **Chemical etching results in the gradual refinement of the as-built surface.** Modifications in morphology were assessed after chemically etching micro-strut samples for 0, 12, 30 and 105min. From a.) strut diameter measurements ($n = 3$ struts; taken as the mean of 100 measurements), and b.) SEM ($\times 100$ (left), and $\times 200$ (right)), it is clear that chemical etching results in the gradual removal of Ti-6Al-4V material from the strut surfaces. Scale bars are equal to 1mm (white), to $100\mu\text{m}$ (red), and to $20\mu\text{m}$ (green).ss

5.3.2 Surface roughness modifications

The surface roughness of as-built SLM fabricated components is a result of the aforementioned surface defects [64], [71], [72], [145], [159]. By removal of these defects using chemical etching, modifications in surface roughness can be expected. Qualitatively,

these improvements were observed using SEM (Fig 5.01.c). We next sought to quantitatively reinforce these observations using WLI.

The R_a and R_z values changed as the etching time was increased (Fig 5.02.a). Surfaces exhibit an initial dramatic decrease in R_a and the R_z values at the 12 minute etching time-point. From the SEM images observed in Fig 5.01, it is clear that this is constituted by the removal of partially adhered powder. After this time point, the reagent contacts the bulk material and improvements in surface roughness begin to stagnate. As the surface becomes smoother, the inherent surface roughness of the bulk material becomes the dominant factor in determining the overall surface roughness. At this point, there is no apparent improvement in the R_a and the R_z value.

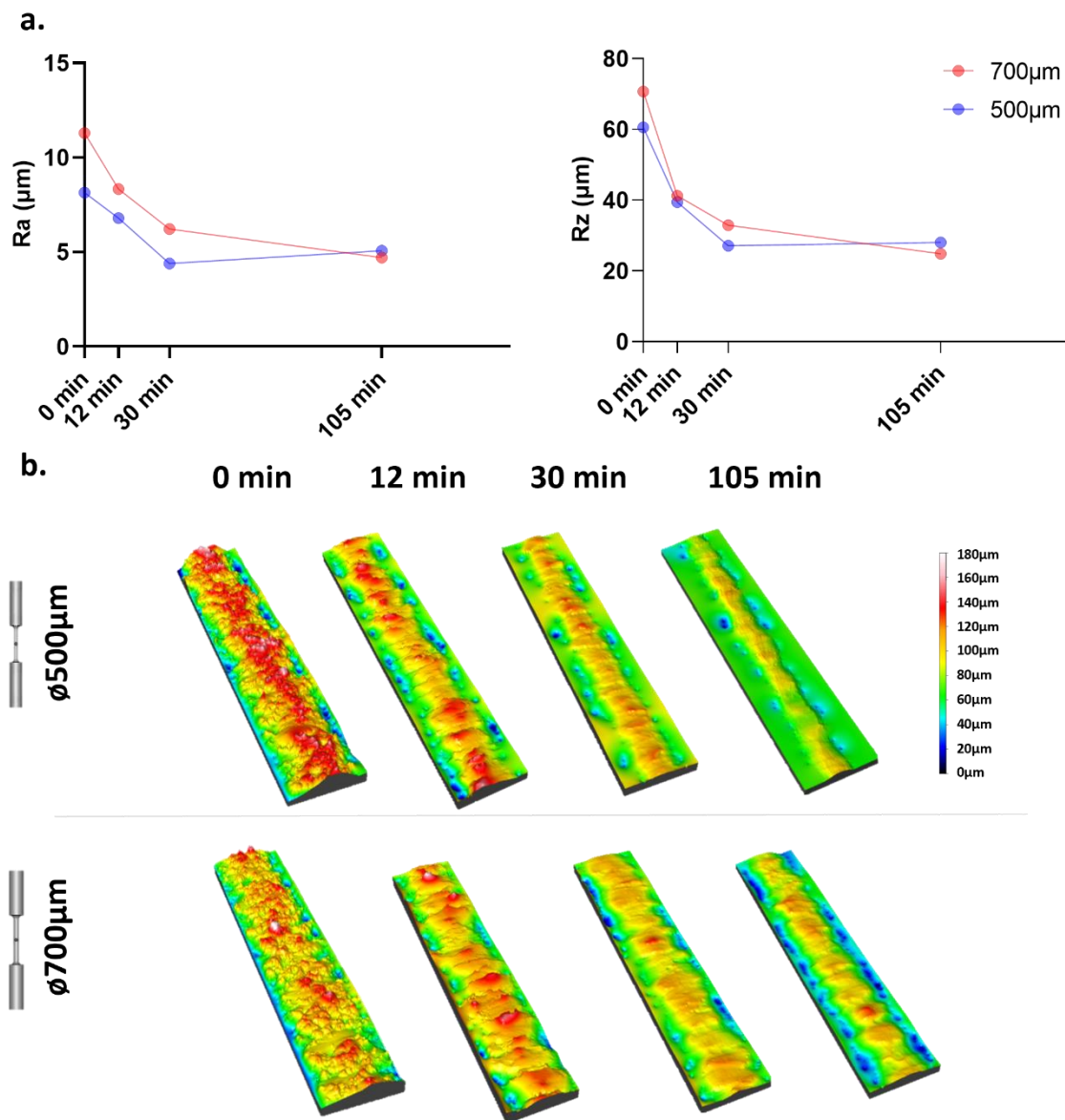


Figure 5.02. **The removal of surface defects using chemical etching is accompanied by a lower surface roughness.** The evolution of surface roughness was characterised using WLI. (b) WLI

reconstructions clearly show the gradual removal of surface inhomogeneities as etching time is increased. a.) The evolution of surface roughness is also quantitatively assessed from WLI R_a and R_z measurements ($n = 3$ samples, taken as the mean of 3 measurements).

At this point of the study, the effects of chemical etching are most apparent after the 12 minute time-point. Once the partially adhered powder has been removed from the strut surface, only a few defects remain on the strut surface and the benefit of continued etching is marginal. Therefore, a decision was made to restrict subsequent testing to the 0 and 12 minute time-points.

5.3.3 Morphological modifications

The presence of surface defects such as partially adhered powder can induce further morphological irregularities in SLM fabricated components [71], [72], [167], [168], [170], [206]. This is particularly important in small-diameter micro-struts as the volume of such defects contributes a significant proportion of the total volume of the strut [71], [72]. By removal of these defects using techniques such as chemical etching, modifications in strut morphology can also be expected.

Micro-strut morphology was assessed using μ CT (Fig 5.03). As described in section 2.7, the mismatch between as-designed and as-fabricated geometries was captured by measuring aspect ratio, strut waviness, and efficient cross-section. In general an improvement in strut morphology can be observed after etching (Fig 5.03). For example, the $\varnothing 500\mu\text{m}$ and $\varnothing 700\mu\text{m}$ struts exhibit a 13.84% and 11.32% in their efficient cross-section (Fig 5.03.c).

Although not the primary focus of this study, a size effect can also be observed. The $\varnothing 700\mu\text{m}$ strut exhibits better morphology compared to the $\varnothing 500\mu\text{m}$ strut. This is apparent both before and after etching. For example, the $\varnothing 700\mu\text{m}$ strut exhibits a 4.59% increase in efficient cross-section before etching, and a 3.01% increase after etching. Similar feature size dependent behaviour has been observed in the literature, and highlights the impact of surface defects in small diameter struts compared to the bulk material [72], [91], [145], [200], [201]. As feature size is reduced, the volume of surface defects contributes a higher proportion of the total volume of the strut. Consequently, a poorer morphology can be observed as strut diameter is decreased.

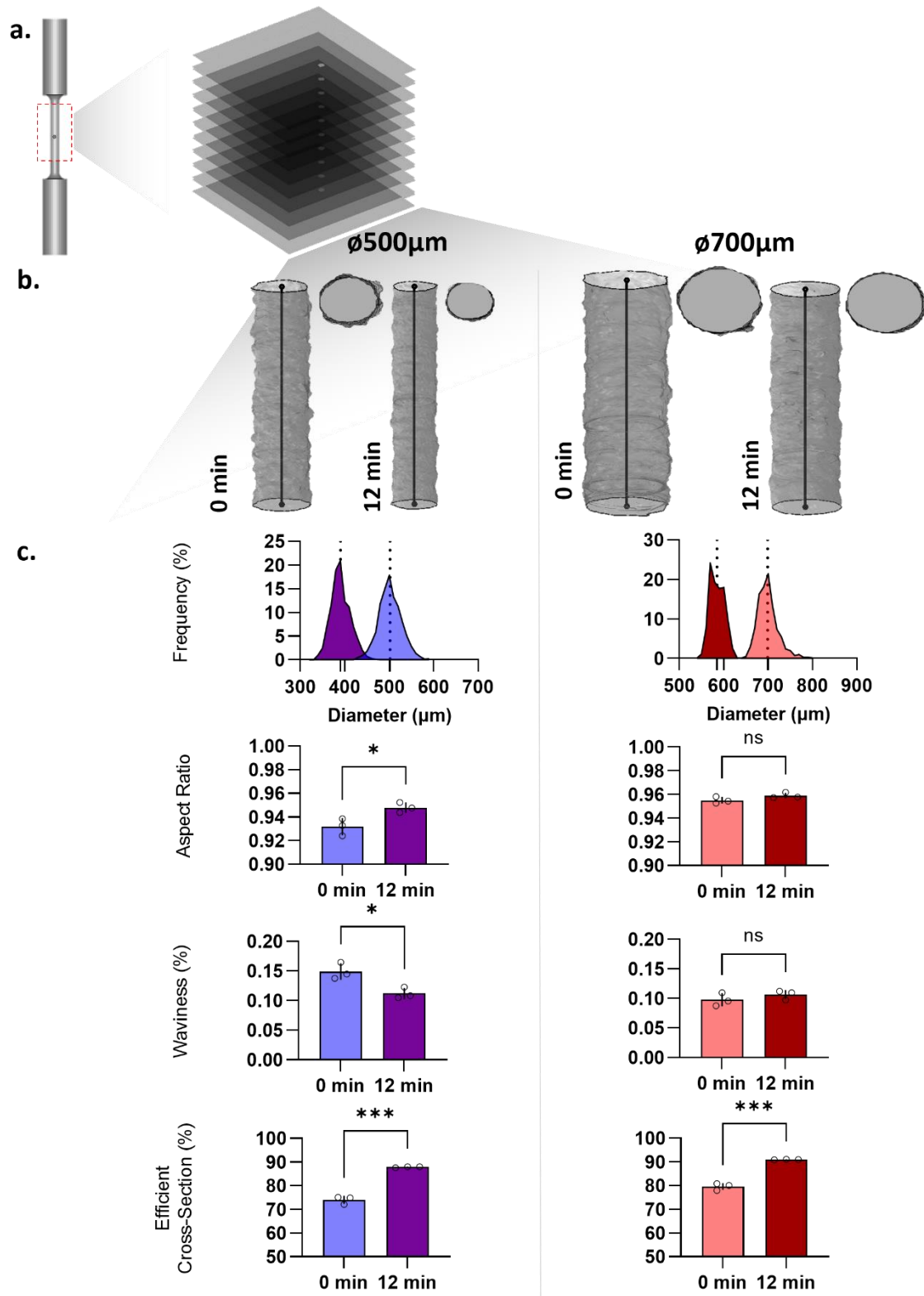


Figure 5.03. **The removal of surface defects using chemical etching leads to improvements in strut morphology.** a.) Micro-strut surface profiles were reconstructed using μ CT. b.) These reconstructions clearly show the evolution of strut morphology after etching. c.) These improvements were quantified by measuring strut diameter, aspect ratio, waviness, and efficient cross-section. All error bars

denote standard deviation, *, **, and *** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$ and *** $p < 0.0002$, student's t -test).

5.3.4 Tensile properties

The mechanical properties of SLM fabricated material is directly influenced by the presence of surface defects [72], [91], [145]. In the as-built condition, this relationship has been shown to be particularly detrimental in small diameter micro-struts [72], [91], [145], [197]. By modification of this surface using chemical etching techniques, modifications in mechanical properties could also be reasonably expected.

Here, the mechanical properties of the micro-strut samples are assessed in uniaxial tension before and after etching (Fig 5.04). Significant improvements can be observed in the etched material for both the $\varnothing 500\mu m$ and $\varnothing 700\mu m$ struts, as assessed by the elastic modulus, yield strength and failure strain (Fig 5.04.c). For example, the yield strength of the $\varnothing 500\mu m$ and $\varnothing 700\mu m$ samples increased by 37.44% and 46.59% respectively following 12 minutes of etching.

As quantified by the elastic modulus, the as-built struts exhibit a significantly lower stiffness than the material in its bulk form. These results coincide with recent studies in the literature where the average elastic modulus of sub-millimetre diameter struts was in the range of 30-85% percent of the bulk material [72], [91], [145], [200], [201]. This effect can be linked to the measurement of cross-sectional area for stress calculations. Near-surface defects such as partially adhered powder are non-load bearing but contribute a significant proportion of the strut diameter [72]. We observed that the efficient cross-section of the as-built struts was only 74% and 79.59% of the mean strut diameter (Fig 5.04). Consequently, measurements of the core load-bearing cross-section is overestimated, and result in a decreased elastic modulus of the strut. Despite this, these defects are inherent to the strut in the as-built condition, and it is necessary to take into account for accurate material characterisation. In the etched struts the majority of defects have been removed and consequently, measurements of the cross-sectional area represent a much larger fraction of load bearing material. An improvement in the efficient cross-section by 13.84% and 11.32% was observed after etching (Fig 5.03). This shows the measured cross-section in the etched struts is much closer to the core load bearing cross-section, and therefore a much higher stiffness is observed.

The as-built struts exhibit a significantly lower yield strength than the bulk material. This also coincides with the literature where the average yield strength of sub-millimetre struts was in the range of 30-85% of the bulk material [72], [91], [145], [200], [201]. Similar to elastic modulus, this can be explained by the large volume of non load bearing material

included in cross-sectional area measurements. It is therefore not surprising that etching led to an increase in yield strength. This is also a consequence of the smaller fraction of the cross-sectional area being attributed to non load bearing surface defects.

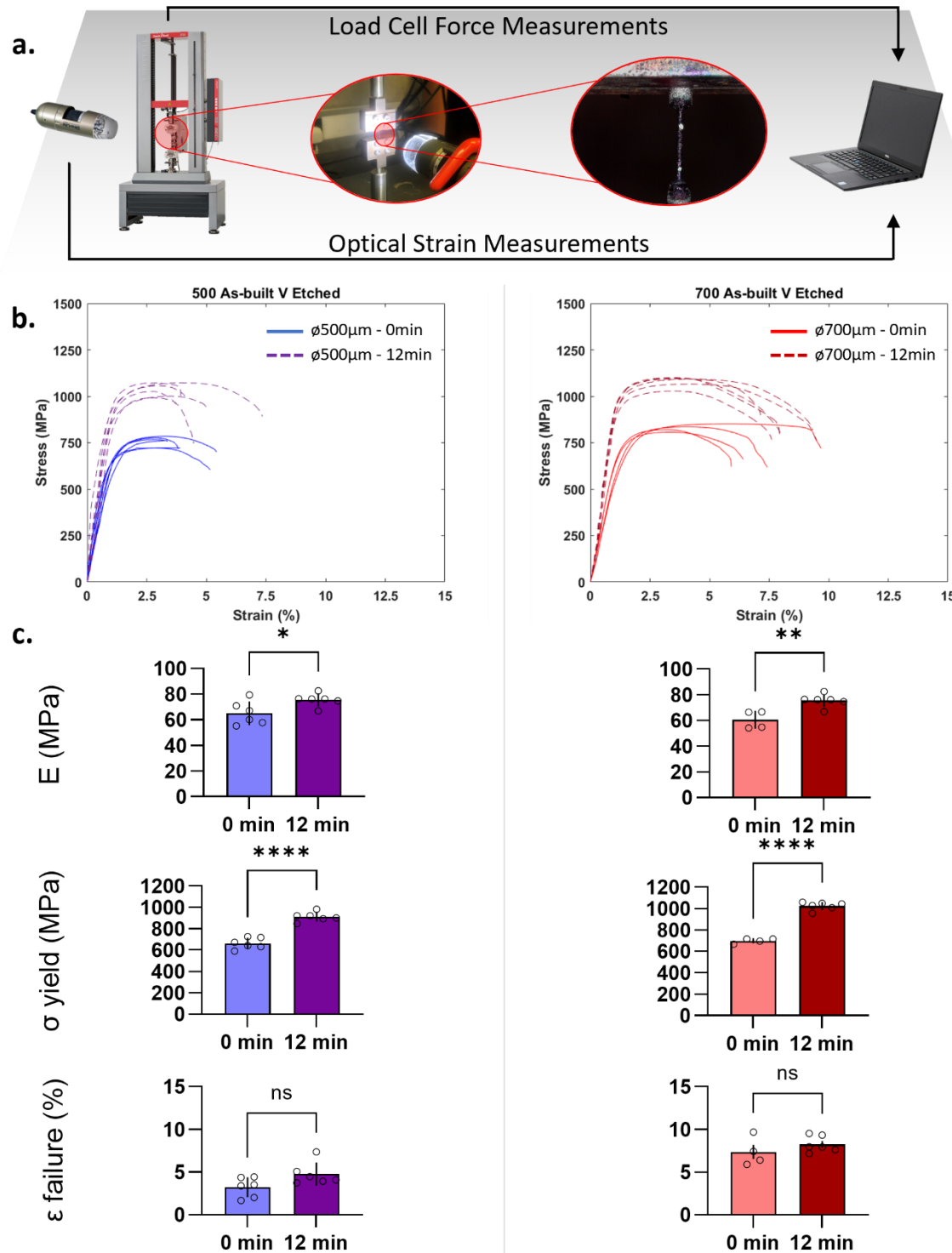
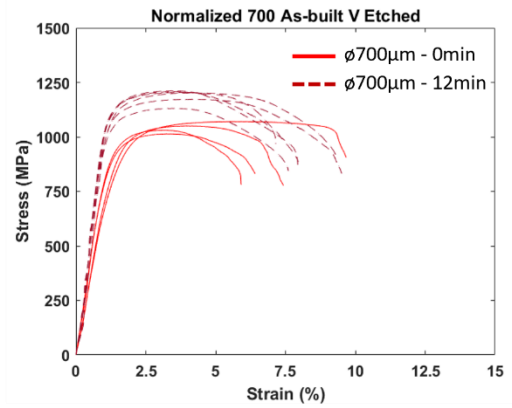
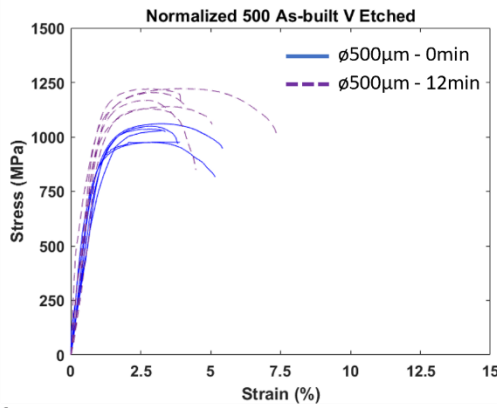


Figure 5.04. **Chemical etching yields improved tensile properties in micro-struts.** a.),b.) Micro-struts samples were pulled to failure in uniaxial tension under displacement control. c.) Improvements in elastic moduli, yield strength, and failure strain could be observed after etching. All error bars denote

standard deviation, *, **, *** and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, student's t -test).

Based off this explanation, the stress-strain curves for each group were normalized to the respective measurements of the efficient cross-section (Fig 5.03). This leads to a larger increase in stress for the as-built groups (Fig 5.05). When analysed in this way, the elastic modulus between as-built and etched groups is more comparable. However, differences in yield strength are still observed, indicating that there are other effects at play. The most obvious explanation is the increase in local stress concentrations due to the rough surface, which is known to reduce strength [207], [208], [209].

a.



b.

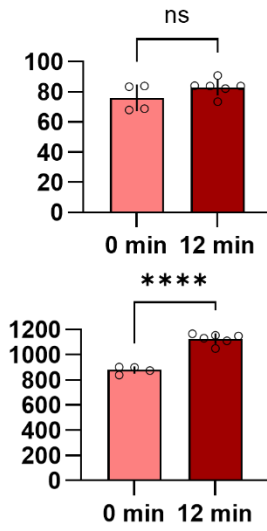
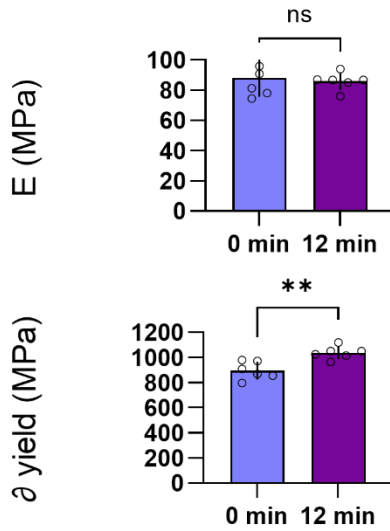


Figure 5.05. **Mechanical properties are affected by morphological defects in micro-struts.** Surface defects inherited from the fabrication process result in a reduction in the efficient cross-section responsible for load-bearing under tension. a.) After normalising the stress-strain curves to the respective measurements of efficient cross section, b.) the increase in elastic and yield strength is less apparent.

After yielding, the material begins to plastically deform [72], [90], [91], [145], [159], [198], [200], [206], [210]. For ductile materials, stress typically continues to increase up to the ultimate tensile strength (UTS). As loading continues past the UTS, the sample necks and

a state of triaxiality is induced at the centre of the sample. During this phase, micro voids grow and coalesce forming large cracks. Stress is concentrated at the tip of cracks and eventually induces a less ductile shearing failure along the axis of maximum principal stress i.e. 45° degree inclination to the load direction [80], [90], [91]. This phase characterises the final failure of the material and is characterised by a drop off in stress after the UTS is reached. In brittle failure, this may occur instantaneously, however in ductile failure may be extended substantially [72], [91], [145], [210]. The ductility of the final failure zone can be inferred by the drop in stress between the ultimate tensile strength and the failure strength (Fig 5.06). For both $\varnothing 500\mu m$ and $\varnothing 700\mu m$ struts, the most significant drop can be observed in the as-built struts. This is characteristic of less ductile failure and can be attributed to the higher density of defects and the subsequent increase in the local stress concentration localised close to the strut surface in the final shear zone. By extension, a reduction in failure strain is also associated with a more brittle fracture (Fig 5.06).

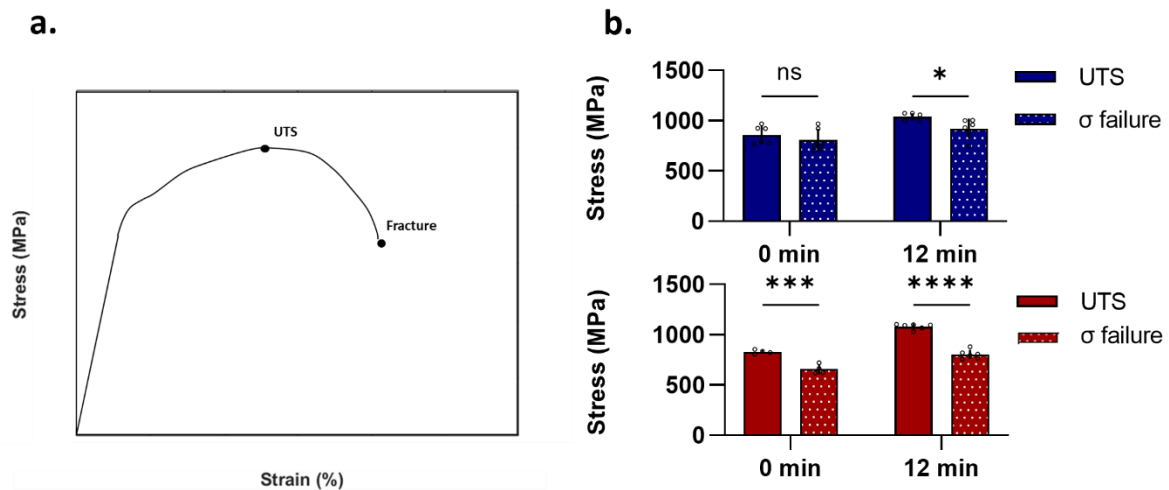


Figure 5.06. **Chemical etching yields increased ductility.** a.) After the UTS, a drop in engineering stress can be attributed to necking. b.) The ductility of failure can be inferred by the difference between the UTS and failure strength. All error bars denote standard deviation, *, **, *** and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, multiple t-test).

SEM was next used to assess the mode of fracture (Fig 5.07). All struts exhibit typical ductile failure characterised by micro-void growth and coalescence normal to the tensile axis (Region I), progressing into a region of shear failure normal to the axis of maximum principal stress (Region II). Despite the significant improvements in elastic modulus and yield strength, there is no obvious difference in the mode of fracture between the as-built and etched struts. This highlights that the improvement in mechanical properties after etching is likely not a result of any fundamental change to the material, but rather a change to the load bearing geometry.

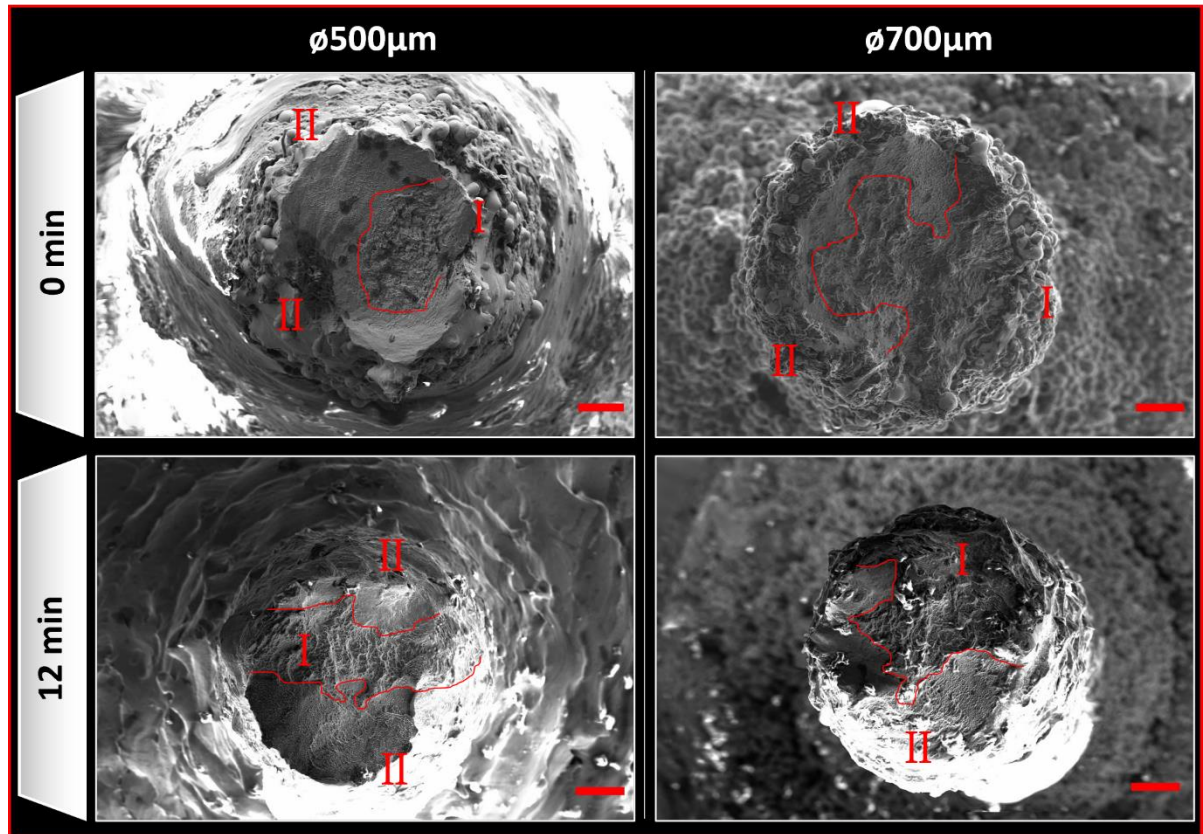


Figure 5.07. **Fracture surfaces indicate ductile failure.** SEM showing representative fracture surfaces before (top) and after (bottom) chemical etching. Both as-built and etched groups exhibit typical ductile failure mechanisms. Failure can be seen progressing from a ductile region of micro-void coalescence (I), into a more brittle shearing mode (II). Scale bars are equal to $100\mu\text{m}$ (red).

5.3.5 Fatigue properties

The mechanical properties of the micro-strut samples were also assessed in fatigue. The fatigue resistance of SLM manufactured components is typically controlled by near-surface defects [23], [24], [101], [109], [110]. Similar to tensile properties, it would be reasonable to assume that modifications in the fatigue properties could be driven by modifications in the surface after etching.

The fatigue properties were measured before and after etching (Fig 5.08). As each sample group showed different yield strengths, the S-N curves were normalised as percentages of the yield strength. This allowed us to capture the entire range of low cycle fatigue (LCF) to high cycle fatigue (HCF).

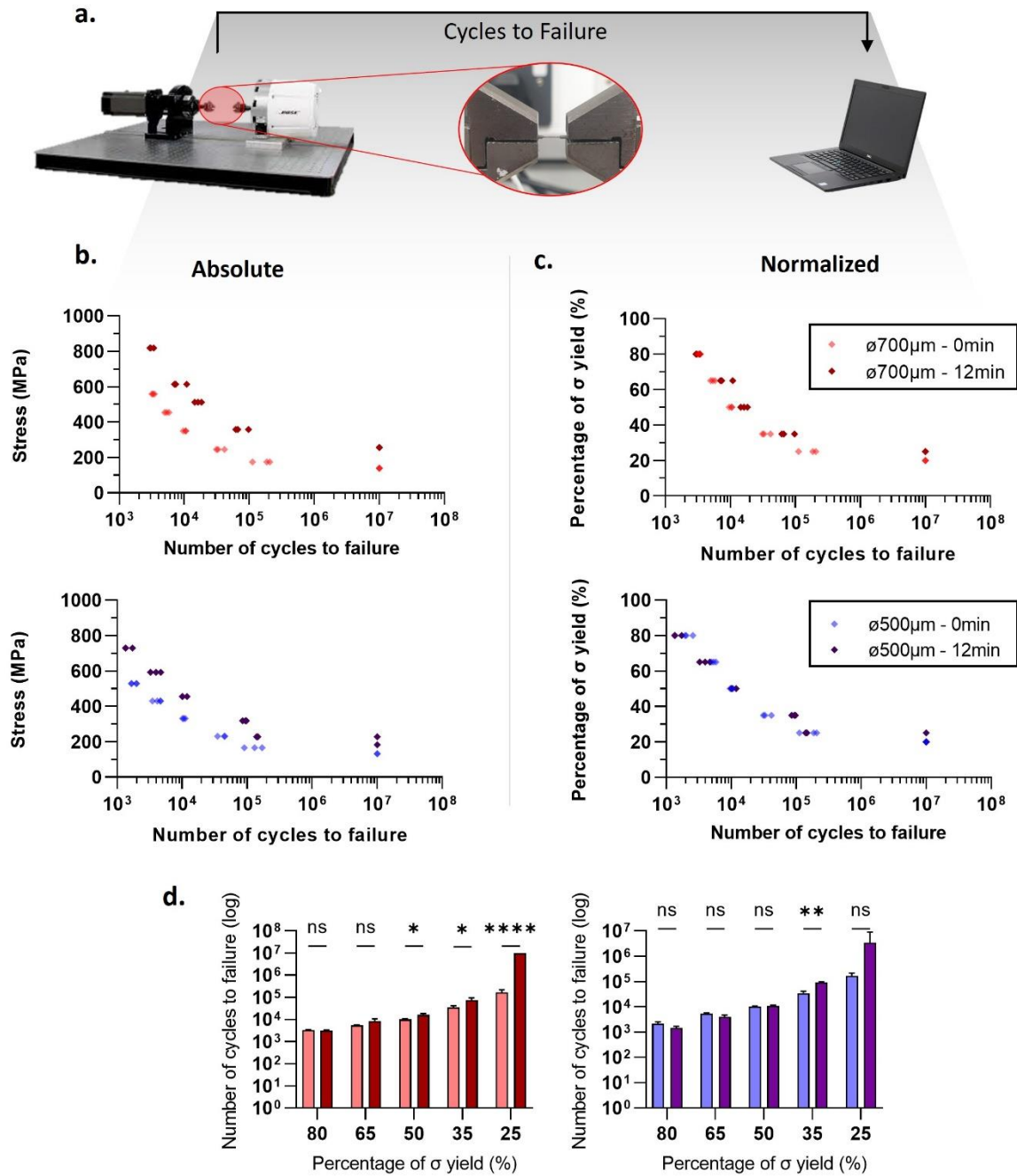


Figure 5.08. **Chemical etching yields improved fatigue properties in HCF loading.** a.) Micro-struts were tested in load controlled tension-tension fatigue at 80, 65, 50, 35, 25, and 20% of the tensile yield strength. The number of cycles to failure was recorded, and plotted against load creating S-N curves. b.) Plotted against absolute stress, the etched group exhibits a higher number of cycles to failure at any given load. c.), d.) However, when stress is normalised to account for differences in tensile strength, the improvement is less apparent as the loading regime progresses towards LCF. All error bars denote standard deviation, *, **, *** and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, student's t -test).

LCF is characterised by the application of high stress, and a short number of cycles to failure [24], [101], [109]. Although an improved resistance to LCF is apparent after etching

when considering absolute stress, a similar number of cycles to failure is exhibited between groups when stress is normalised to the respective yield strengths. This indicates that the increased resistance to LCF is limited to the effects of yielding. At the other end of the S-N curve, HCF is characterised by the application of a relatively lower stress and a larger number of cycles to failure [24], [101], [109]. As testing progresses from LCF to HCF, the etched struts exhibit an increasing number of cycles to failure than the as-built struts (Fig 5.08.b). At the far end of this zone, the fatigue limit is defined as the fatigue stress range when specimens survive 10^7 cycles [101], [109]. Here, the etched struts exhibit a higher fatigue limit than the as-built struts. This can also be observed statistically in Fig 5.08.d. However, given the small n number ($n=3$) for each test, this analysis may carry less weight than a simple interpretation from the overarching S-N curve as a whole (Fig 5.08.c). These trends are apparent when absolute stress is considered, but also when it is normalised to the yield strength. As resistance to HCF is predominantly derived from resistance to crack nucleation, these results suggest lower surface stress concentrations in the etched group, making it more difficult for a crack to nucleate. Consequently, stress concentrations around surface defects play a significant role in the resistance to HCF fatigue, and are indicative of effects beyond yielding.

For both LCF and HCF, fatigue cracks generally nucleate from stress concentrations around the surface or near surface defects [23], [24], [101], [109], [110]. For LCF, the applied cyclic stress is high enough to initiate crack nucleation at a larger number of such sites [101]. Here, the energy needed to open a crack is likely independent of any differences in the as-built and etched surfaces. In other words, there are still a large number of defects on the etched surface from which a crack can just as easily nucleate under LCF loading conditions. Potential sites of the critical crack nucleation are marked by a green arrow (Fig 5.09). No different to the as-built group, such sites on the etched samples have their origin in a defect lying on the strut surface. The progression of the crack into the crack growth zone is indicated by river markings propagated from the crack nucleation site. As the crack grows, it is characterised by predominantly plastic deformation and resistance is derived from local material properties at the crack tip [24], [101]. It is therefore unsurprising that both groups continue to behave similarly in this phase. Here, secondary micro-cracks can be observed ahead of the crack tip (Fig 5.10). This is characteristic of the material's fatigue resistance, acting to consume energy for crack propagation [24]. Due to relatively large stressing cycles inherent to LCF, the crack can only be maintained in stable growth for a short number of cycles until failure [101]. In this regard, LCF fracture surfaces are typically characterised by a small crack growth zone, and relatively larger zone of instantaneous failure [23], [24], [101], [109], [110]. Indicative of a similar resistance in the crack growth phase, these zones are comparable for as-built and etched samples.

Similar to LCF, this bears explanation in the energy needed to initiate a crack. In HCF, the cyclic stress is much lower and fewer defects are activated as possible sites of crack nucleation. As a result, the density of defects between the two groups is a relevant factor, and consequently, a larger number of stress cycles are required to nucleate a crack in the etched group. As crack growth continues, however, a similar response can be noted between the two groups. In HCF crack growth, a much smaller plastic zone exists at the crack tip, and as a result, HCF is characterised by predominantly elastic behaviour [101]. However, similar to LCF, crack growth resistance is derived from the local material properties and hence it is unsurprising that both groups exhibit a similar fracture surface. Here, secondary micro-cracks can also be observed ahead of the crack tip (Fig 5.10). However, these are much smaller than those observed in the LCF regime, and indicative of the smaller plastic zone at the crack tip. Due to relatively lower stressing cycles inherent to the HCF regime, the crack can be maintained in stable growth for a larger number of cycles until failure. Consequently, HCF fracture surfaces are typically characterised by a larger crack growth zone, and smaller zone of instantaneous failure than that observed under LCF loading. Similar to LCF, near proportional zones for as-built and etched samples indicate a similar resistance in the crack growth phase.

These observations have been interpreted from the normalised S-N curve (Fig 5.08.c). However, the actual operating stress in each step is quite different between samples (Fig 5.08.b). This is because the yield strength of each sample group is also different.

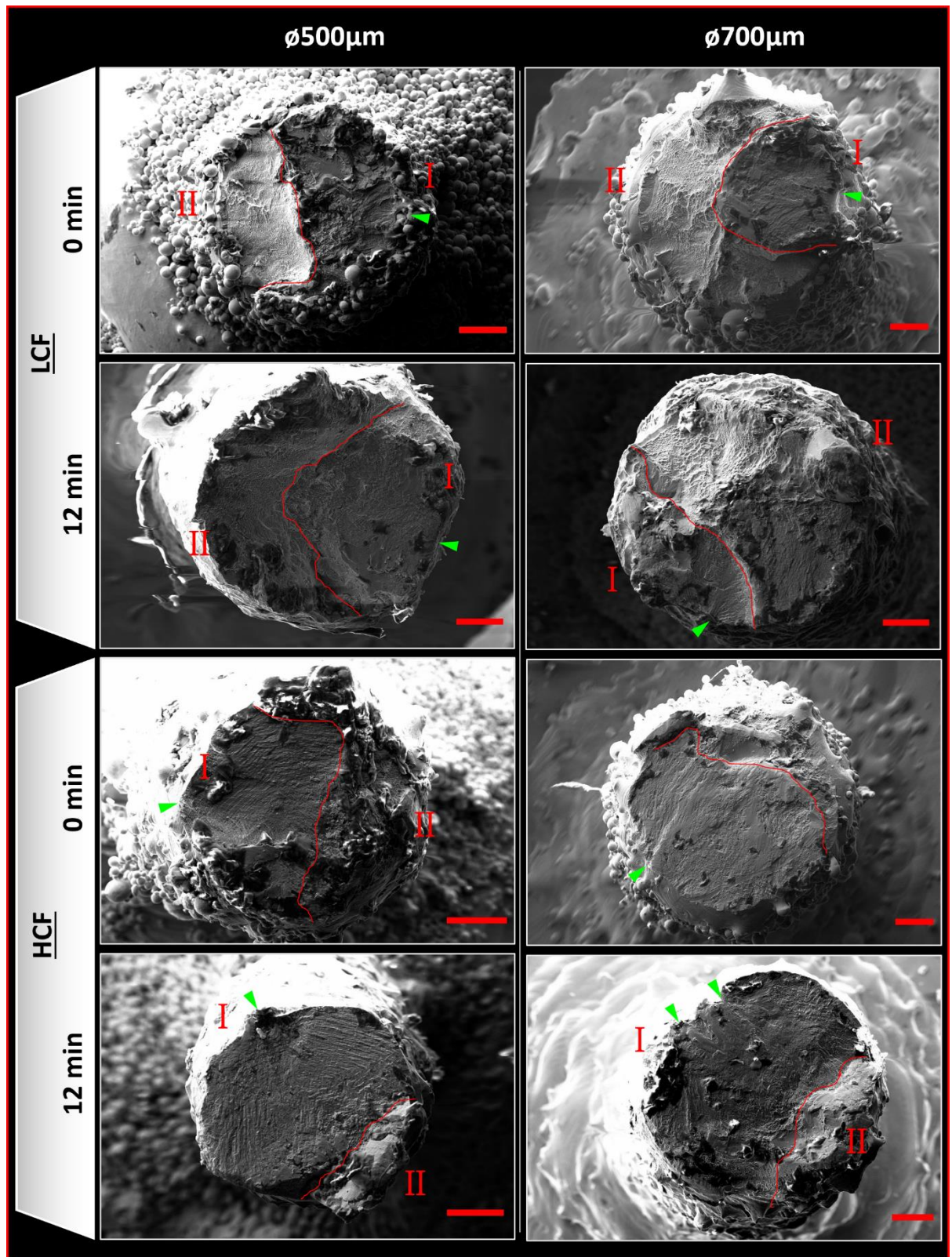


Figure 5.09. **Cracks initiate in surface and near-surface defects.** SEM showing representative fracture surfaces for as-built and etched groups. Crack initiation can be generally located in surface and near-surface defects in both LCF, and HCF fatigue loading regimes. Potential sites for crack initiation are indicated by a green arrow. The crack growth, and final fracture zones are labelled Regions I and II respectively. Scale bars are equal to 100 μm (red).

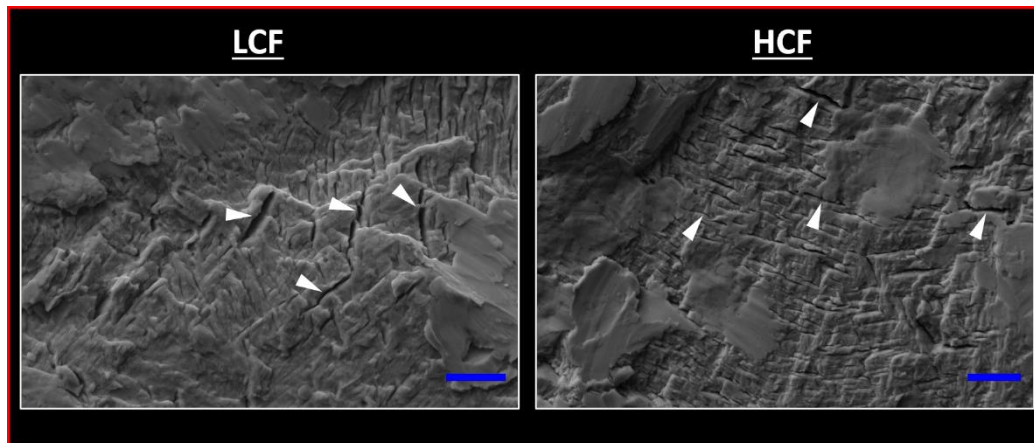


Figure 5.10. The crack growth zone is characterised by secondary micro-cracks. SEM showing representative crack growth zones on the fracture surface in LCF and HCF loading. Secondary micro-cracks are indicated by white arrows. Scale bars are equal to $10\mu\text{m}$ (blue).

5.3.6 Chemical etched lattice structures

Chemical etching was also applied to full lattice structures. Here, the mechanical properties of the samples are assessed in compression (Fig 5.11). In this instance, mechanical properties are dictated by both the material properties of the individual struts, and the lattice design. In this regard, improvements in material properties are not directly measured, but rather inferred by improvements in the engineering mechanical properties. As a result, comparison between as-built and etched groups is only possible if the lattice design is kept constant. As this extends to strut diameter, the etched group was printed with slightly thicker struts. After etching, this ensured a fair comparison with the as-built group (Fig 5.11.d).

Generally, the mechanical properties of the lattice improve after etching (Fig 5.11.b & 5.11.c). Although not significant, the etched group exhibits a higher stiffness than the as-built group. Similar to micro-strut samples, this can be related to the proportion of material that is load bearing. Due to the higher density of defects in the as-built lattice, a larger proportion of material is non load bearing and consequently results in a decreased elastic modulus. For the same reason, significant improvements in the yield strength and UTS can also be achieved after etching.

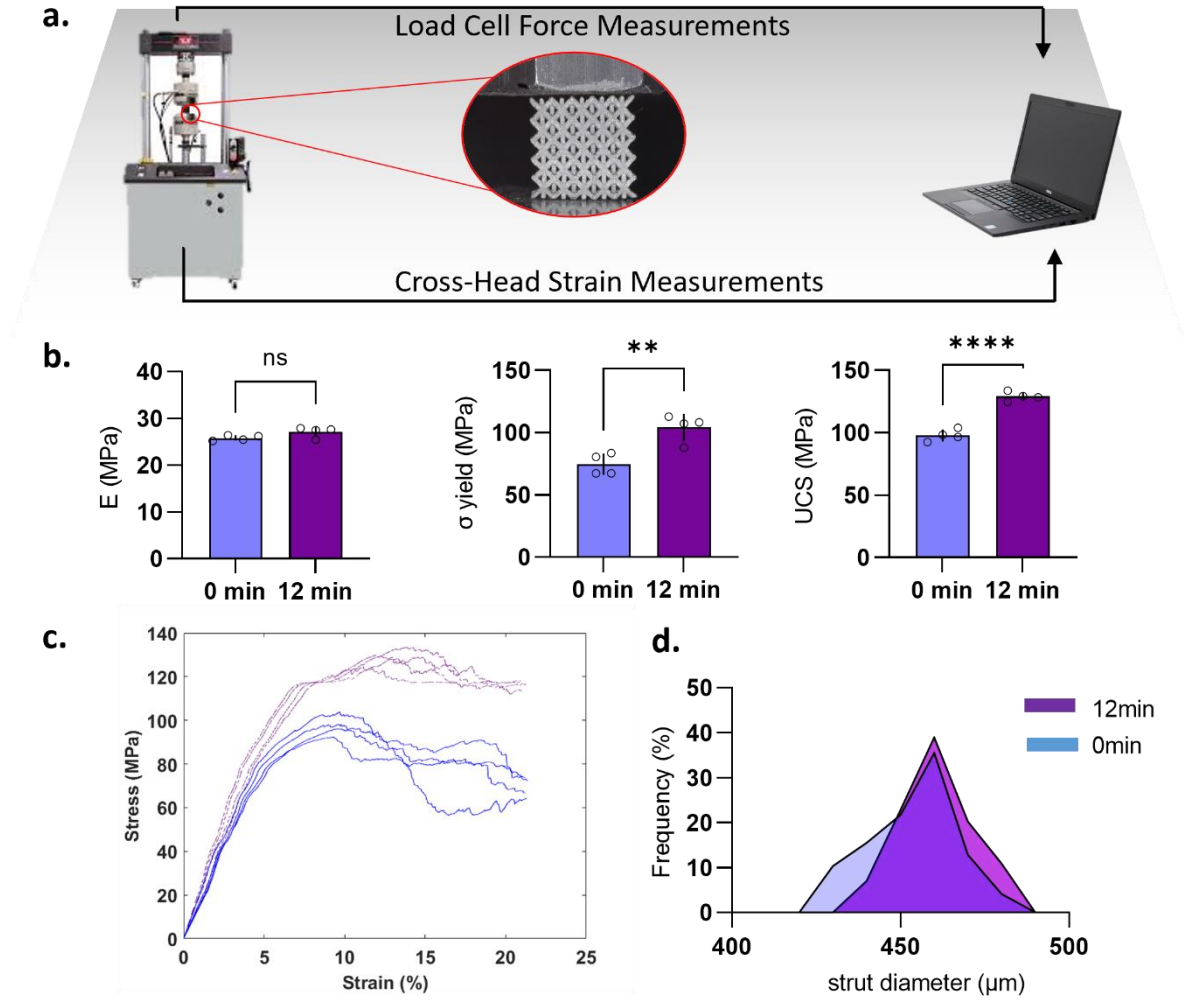


Figure 5.11. **Improved Mechanical Properties of Individual Micro-struts translates to full lattices.** a.), c.) As-built and etched lattices were then compressed uniaxially under displacement control until collapse. b.) Improvements in elastic moduli, yield strength, and ultimate compressive strength could be observed after chemical etching. (d) Comparison of zz-orientated struts. All error bars denote standard deviation, *, **, *** and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, student's t -test).

5.4 Conclusion

In this work, the potential benefits of chemically etching additively manufactured Ti-6Al-4V lattices in a solution of HF and HNO_3 was investigated. By using micro-strut dog-bone samples, geometrical variations between lattice designs could be isolated, allowing us to characterise the properties of the bulk material.

Chemical etching was successfully used for the removal of surface defects from the as-built material. This resulted in significant improvements in surface roughness and strut morphology. The efficacy of this process was at least partially dependent on the initial state of the surface. Using an incremental etching approach, the most apparent improvements

in these qualities could be observed at the initial time point when the frequency of defects was high. As etching continued, subsequent improvements were less apparent.

The etched material exhibited a significant improvement in tensile strength and elastic modulus. This was related with the improved strut morphology achieved by etching. In the as-built material, surface defects such as partially adhered powder are non-load bearing, yet represent a significant proportion of the material volume. Consequently, removal of such defects after etching results in a higher fraction of load bearing material in any given cross-section, and subsequently an increase in strength and elastic modulus. Analysis of fracture surfaces supported this conclusion. No apparent discrepancy between failure mechanisms could be observed between groups, supporting a change in the load bearing geometry, rather than the material properties.

An increase in failure strain was also observed after etching. Local stress concentrations around surface defects drive accelerated failure in the final shear zone, consequently resulting in a more brittle failure and lower failure strain.

Improvements in mechanical properties also extended to fatigue. Here, the most apparent improvement could be observed in the HCF regime. As HCF is particularly sensitive to discrepancies in near surface stress concentrations, the improved fatigue resistance after etching can be related to the improvement in surface roughness. Analysis of fracture surfaces supported this conclusion. After crack nucleation, fracture surfaces between groups appear similar in both LCF and HCF, indicating a similar resistance to crack growth by the bulk material.

Chapter 6: Chemical etching of additively manufactured Ti-6Al-4V biomaterials enhances mesenchymal stromal cell mineralization

This chapter has been published in the Journal of 'Biomedical Materials Research: Part A', under the title 'Chemical etching of Ti-6Al-4V biomaterials fabricated by selective laser melting enhances mesenchymal stromal cell mineralisation', and is co-authored by Conor O'Keeffe, Marcin Kotlarz, Ines F Gonçalves, Caitríona Lally and Daniel J Kelly.

MSCs were supplied by University College Dublin. M, K supported cell culture. I.F, G performed RNA isolations and PCR analysis. C, L and D.J, K supervised this work.

Abstract

Porous titanium scaffolds fabricated by powder bed fusion additive manufacturing techniques have been widely adopted for orthopaedic and bone tissue engineering applications. Despite the many advantages of this approach, topological defects inherited from the fabrication process are well understood to negatively affect mechanical properties and pose a high risk if dislodged after implantation. Consequently, there is a need for further post-process surface cleaning. Traditional techniques such as grinding or polishing are not suited to lattice structures, due to lack of a line of sight to internal features. Chemical etching is a promising alternative; however it remains unclear if changes to surface properties associated with such protocols will influence how cells respond to the material surface. In this study, we explored the response of bone marrow derived mesenchymal stem/stromal cells (MSCs) to Ti-6Al-4V whose surface was exposed to different durations of chemical etching. Cell morphology was influenced by local topological features inherited from the SLM fabrication process. On the as-built surface, topological non-homogeneities such as partially adhered powder drove a stretched anisotropic cellular morphology, with large areas of the cell suspended across the non-homogeneous powder interface. As the etching process was continued, surface defects were gradually removed, and cell morphology appeared more isotropic and was suggestive of MSC differentiation along an osteoblastic lineage. This was accompanied by more extensive mineralisation, indicative of progression along an osteogenic pathway. These findings point to the benefit of post-process chemical etching of additively manufactured Ti-6Al-4V biomaterials targeting orthopaedic applications.

6.1 Introduction

Powder bed fusion (PBF) is an additive manufacturing technique which has enabled the fabrication of geometrically complex metallic structures [211], [212]. The basis of this technology is the selective consolidation of thin layers of metallic powders via processing

with a focused high energy laser beam based on a computer aided design model. Among these technologies, selective laser melting (SLM) is arguably more suited to small feature resolution [10], [11], [183], [184]. This has lent itself well to the fabrication of intricate porous metallic lattice structures [11]. Applied to biomedical implants, these lattices offer advantages over traditional non-porous implants by allowing bone in-growth and more closely recapitulating native tissue stiffness gradients [8], [9], [46], [213]. Osteointegration and the overall success of orthopaedic implants is driven by cellular responses at the implant surface. The surface topology of the implant plays an important role in mediating cell behaviour [21]. Topological features act as biophysical stimuli which are recognised by cells and converted into a cellular response *via* mechanotransduction. This occurs through the activation of complex signalling pathways, rooted in the relay of stimuli through integrin activity, stretch activated ion-channels, or cell-surface receptor proteins. Ultimately, these pathways regulate gene transcription to control cellular functions and phenotypes [21], [112], [113], [114]. In light of these factors, surface topology is a crucial design consideration for modulating cell behaviours in biomedical implants and tissue engineering strategies. Surface roughness is an important topological feature which has been shown to mediate cell behaviour [21], [25]. Despite no consensus on an ideal value, it is becoming apparent that both overly rough and overly smooth surfaces are not ideal for osteogenic differentiation [21], [25]. On excessively rough surfaces, cells may adapt to minimise contact with high energy topological discontinuities, consequently hindering mechanotransductive factors such as f-actin formation or cell spreading [21], [25]. On the other hand, excessively smooth surfaces may not provide enough topological features to modulate the actin cytoskeleton and activate associated mechanosensitive signalling pathways [21], [25], [115].

The surface of SLM fabricated components is inherently rough [64], [71], [72], [141], [159], [214]. Powder granule size and morphology combined with the physics of the melt pool result in partially adhered powder on external surfaces [64]. This occurs in varying degrees as a result of factors such as geometrical design and printing parameters. This likely contributes to the varied cell-substrate interactions reported in the literature [215], [216]. Furthermore, the presence of such topological defects is well understood to detrimentally affect mechanical properties, and pose a high risk if dislodged after implantation [22], [23], [24], [110], [141], [145]. Consequently, whether the as-built surface is beneficial to osteointegration or not, there is a need for further post-processing surface cleaning steps. For traditional non-porous SLM fabricated components, a range of treatment options are available, such as abrasive blasting or mechanical polishing [115], [139]. The effect of these treatments on subsequent cellular responses is unclear [22]. On the one hand, the as-built surface has been shown to be excessively rough for osteogenic differentiation, and better

results have been observed after post-process surface cleaning [22], [139], [217], [218]. On the other hand, surface cleaning can also lead to unfavourably smooth surfaces, with superior results observed on the rough as-built surface before any post processing [219], [220]. Despite no consensus on an ideal roughness value, it is clear that both excessively rough and excessively smooth surfaces can impede bone differentiation, motivating the implementation of systematic studies to identify appropriate surface treatments [21], [25]. For additively manufactured metal surfaces, such studies are still lacking.

Surface cleaning is more complicated for lattice structures, as the aforementioned traditional line of sight techniques are unsuitable for materials with complex architectures and internal features. In such cases, chemical etching is proving a suitable alternative [140], [190], [191], [221]. Applied to titanium alloys, hydrofluoric acid (*HF*) is most commonly employed as an effective etching reagent, removing material by readily reacting with Ti to form Ti hexafluoride complexes and hydrogen gas [187], [193], [194], [204]. In our previous work, we showed this technique could achieve a spectrum of topologies, using an incremental approach which gradually refined the material surface [141]. After continued etching, surface defects could be entirely removed, revealing a smooth, defect-free surface more representative of the bulk material. We further demonstrated that improvements in the structural and mechanical properties of as-built lattice structures can be achieved *via* such etching strategies. These improvements are directly related to the removal of surface defects, and are achieved incrementally, with better results observed after longer etching times. It remains unclear, however, if changes to surface properties associated with such chemical etching protocols will influence how cells respond to the material surface. In addition to mechanical properties, the cellular response will be critical to the overall success of metallic orthopaedic implants and scaffolds developed using SLM. Therefore, the goal of this study was to engineer a spectrum of topologies by gradually refining the surface of SLM fabricated Ti-6Al-4V using an incremental *HF/HNO₃* etching process. Bone marrow derived mesenchymal stem/stromal cells (MSCs) were then seeded onto each surface, and the cell-substrate interactions were analysed. This analysis was performed for both a simple flat plate geometry and a more clinically relevant grid-like lattice structure.

6.2 Methods

6.2.1 Design & manufacturing

Two sample groups including 1.) a plate and 2.) a grid, were ideated (Fig 6.01). Within each group, sub-groups were created to account for the evolution of surface topology as an as-built SLM surface is gradually chemically etched towards a smooth surface.

Both groups were designed using the computer-aided-design (CAD) software Autodesk Netfab. For the plate group, all post-etching sub-groups (P0, P12, P30 and P105) were derived from Plate Design 1. For the grid group, three different variations of this design (Grid Design 1 - 3) were used, with the intention of having sub-groups (G0, G12 and G30) at each etching time-point (0, 12 and 30 minutes) with comparable strut diameters. Therefore, struts in the G0 group were designed as $\varnothing 500\mu\text{m}$, whereas struts in the G12 and G30 groups were designed slightly thicker as $\varnothing 520\mu\text{m}$ and $\varnothing 550\mu\text{m}$ respectively. This also led to a post-etching pore size of $500 \times 500\mu\text{m}$ in each group.

All samples were built using a Realiser SLM 50 manufacturing system (spot size = $160\mu\text{m}$) and Ti6Al4V, Grade 23 (particle size = $24.5\text{-}55\mu\text{m}$) powder under an argon controlled atmosphere ($\text{o}_2 < 0.2\%$). Powder size was measured with a Malvern Instruments Mastersizer 2000 by laser diffraction. The CAD geometry was processed in $0.25\mu\text{m}$ slices, using a contour-and-hatch (C&H) laser scanning strategy. C&H and laser parameters were adopted from Chapter 3.

After printing, samples were removed from the build plate using electrical discharge machining (EDM) and sonicated in an alcohol solution for 30 minutes to remove loose powder.

6.2.2 Chemical etching

Samples were incrementally chemical etched in a mixture of *HF* and *HN*O₃ (Kroll's Etching Reagent, Labquip) with the intention of having sub-groups accounting for the evolution of surface topology as surface defects inherited from the fabrication process were gradually removed. This resulted in four plate subgroups, namely P0, P12, P30 and P105 etched for 0, 12, 30 and 105 minutes respectively, and in three grid subgroups, namely G0, G12, G30 and G105 etched for 0, 12 and 30 minutes respectively.

After etching, samples were sonicated in isopropyl alcohol for 30 minutes, submerged in deionised water for 30 minutes, and left to dry at room temperature.

Brightfield microscopy was used to ensure consistent strut diameter across P0, P12 and P105 groups. Micrographs of the strut sections were acquired at 5.6x magnification using an Olympus SZX7 stereomicroscope, and strut diameter was measured in the programming software MATLAB using a thresholding technique to extract a boundary profile of the strut, and subsequently measuring the diameter across a number of points perpendicular the centroidal axis.

6.2.3 Scanning electron microscopy – metal surfaces

Characterisation of surface topologies was assessed using SEM. Images were taken using a Zeiss ULTRA SEM microscope and SE2 detector with 60µm aperture, 15kV excitation voltage and 12mm working distance.

6.2.4 Surface roughness measurements

Surface roughness was characterised using white light interferometry (WLI). Measurements were taken at 50x magnification, and used to calculate surface roughness, quantified by the S_a and S_z values in accordance with ISO 4287.

6.2.5 Cell culture

Bone marrow derived MSCs (MSCs) were harvested from the sternum of adult, female, Saanen goats according to previously established laboratory protocols. This was approved by the University College Dublin Animal Research Ethics Committee (Approval number – AREC 18-17) and the Irish Health Products Regulatory Authority (Approval number – AE18982/P42). MSCs were expanded in the expansion medium Dulbecco's modified eagle's medium (hgDMEM) GlutaMAX supplemented with 10% v/v fetal bovine serum (FBS), 100 U/mL penicillin, 100 µg/mL streptomycin (all Gibco, Biosciences)

MSCs (passage 3) were seeded onto Ti-6Al-4V samples (soaked in media for 2 h prior to seeding) that were placed in agarose coated 48-well plates, at a density of 60,000 cells/sample. These constructs were cultured in the expansion medium for 7 days, followed by 14 days of incubation in the osteogenic medium. The osteogenic medium was composed of the expansion medium supplemented additionally with 100nM dexamethasone, 10mM *β-glycerol phosphate* and 0.05mM *ascorbic acid* (all Sigma Aldrich).

6.2.6 Live/dead imaging

Cell viability was assessed qualitatively using Live/Dead assay (ThermoFisher Scientific) according to the manufacturer's instructions. Samples on days 1, 3 and 7 were washed in Dulbecco's phosphate buffered saline (DPBS), followed by incubation in DPBS containing 1µM calcein acetoxymethyl (calcein AM) and 4µM ethidium homodimer-1 (EthD-1) under light protected conditions for 30 minutes. Samples were then washed again in PBS, before imaging at 20x on a Leica SP8 inverted confocal microscope, excited at 494 and 528nm.

6.2.7 Cell Proliferation Assay

Cell proliferation was assessed by quantifying DNA content using a Quant-iT Pico Green dsDNA assay kit (Invitrogen) according to the manufacturer's guidelines. Samples were washed in DPBS and frozen at -80°C on days 1, 3, 7 and 21. Cellular content from samples

was lysed by incubation in 0.2% Triton X-100 solution in ddH₂O on an orbital shaker for 2 hours. 100 µL Pico Green solution was added to 100 µL sample lysate and incubated for 10 minutes under light protection, and measured using a BioTek Synergy HTX microplate reader at 485nm excitation and 528 nm emission.

6.2.8 Immunofluorescence staining

Samples on days 1, 3, 7 and 21 were fixed in 4% paraformaldehyde (PFA) overnight and then washed in DPBS. Before staining, the constructs were permeabilised in 0.1% TWEEN 20 in DPBS, and incubated in a blocking solution composed of 2% (w/v) bovine serum albumin (BSA) for 30 minutes at room temperature.

A primary anti-body for vinculin (ab18058, Abcam) was prepared at 1:50 dilution in the blocking solution and the samples were incubated in the solution 1h at room temperature. From this point, all subsequent steps were conducted under light protected conditions. Samples were washed in DPBS, and the secondary antibody (Goat Anti-MOUSE Alexa Flour 488, ThermoFisher) in DPBS at a concentration of 1:500, for 1 h. Subsequently, samples were washed again and stained for F-actin (phalloidin-tetramethyl rhodamine B isothiocyanate peptide, ThermoFisher) in PBS at a concentration of 1:40, for 1 h. Finally, samples were washed and stained using DAPI (4,6-diamidino-2-phenylindole solution, Sigma-Aldrich) in PBS at a concentration of 1:500, for 20 min. Images were taken on a Leica SP8 inverted confocal microscope at 20x.

6.2.9 Scanning electron microscopy and energy dispersive X-ray spectroscopy – cells

Samples were fixed in 3% glutaraldehyde solution overnight, dehydrated in a graded ethanol series (25, 50, 75, 90 and 100%) and immersed in hexamethyldisilazane. After drying, samples were mounted on SEM pin stubs with carbon adhesive discs and coated with gold/palladium for 30 seconds at a current of 40 mA using a Cressington 208HR sputter coater. Images were taken using a Zeiss ULTRA SEM microscope and SE2 detector with 60µm aperture, 7.5kV excitation voltage and 5mm working distance. Imaging was coupled with elemental identification using a 20mm² Oxford Inca EDX detector.

6.2.10 Alizarin red staining

Alizarin red powder (Sigma Aldrich) was dissolved at 2% (w/v) concentration in distilled water, the pH was adjusted within a range of 4.1-4.3 and filtered (40 µm). The mineralisation was assessed on day 21. The samples were incubated in the alizarin red solution for 30 minutes whilst being shaken. Samples were then washed 5 times with shaking in distilled water, and allowed to dry before imaging at 1.2x and 3.2x using

brightfield microscopy (Olympus SZX7). Acellular samples were used as controls to exclude any nonspecific binding of alizarin red to the metallic surfaces.

6.2.11 RNA isolation and quantitative real-time PCR

Samples were washed in PBS before snap freezing and kept in -80°C until additional process. RNA was isolated via Trizol method (Sigma-Aldrich) followed by chloroform extraction and isopropanol precipitation as per the manufacturer's instructions. RNA was re-suspended in RNA free water, and 500ng of RNA was immediately reverse transcribed into cDNA with a high-capacity cDNA reverse transcription kit (ThermoFisher). The levels of gene expression were measured with real-time PCR (Applied Biosystems) using SYBR green master mix (Applied Biosystems) and caprine specific primers (Table 6.01). method and normalized to the arithmetic average of 2 housekeeping genes PGK1 and RPL19.

Table 6.01. List of specific primers for real-time PCR. Cadherin 11 (CDH11) and focal adhesion kinase (FAK) were identified as potential targets associated with adhesion, and runt related-transcription factor 2 (RUNX2), Osteopontin (SPP1), and Bone Sialoprotein (IBSP) with osteogenic differentiation. Phosphoglycerate kinase 1 (PGK1) and Ribosomal protein L19 (RPL19) are housekeeping genes.

Gene name	Gene full name	Forward/Reverse
CDH11	Cadherin 11	F:5' GTACCCACGTTGGACCTCTC 3' R:5' TACCTCCCCAGAGCATCCAT 3'
FAK	Protein tyrosine kinase 2	F:5' CCACCGAGTCCCCTACTACA 3' R:5' TGGTATTACGTGGTGCTGGG 3'
RUNX2	Runt-related transcription factor 2	F:5' GAGTCAAAGCGGGGTGAGAA 3' R:5' CTCCTTTCAACCACGTCGGA 3'
SSP1	Osteopontin	F:5' GGCTACCACATTACAAAATCATCA3' R:5' AGATCCAGGGCTGATGTCCT 3'
IBSP	Bone Sialoprotein	F:5' TCACAGACTTCACATACTAGGGG 3' R:5' GGGTGCTACACGTTGTGAGA 3'
PGK1	Phosphoglycerate kinase 1	F:5' AGCCTTCCGAGCTTCACTTT 3' R:5' AAACCTCCAGCCTTCTTTGGCA 3'
RPL19	Ribosomal protein L19	F:5' CTTGTACACACCCACGCTCC 3' R:5' CAATTGCCGAGGCCACTATG 3'

6.2.12 Statistical analysis

Statistical analysis was performed using the software package GraphPad Prism. Statistical tests used to compare groups are indicated in figure legends. Significance was accepted at a level of $p < 0.05$. Results are expressed as mean $\pm$ standard deviation.

6.3 Results and discussion

6.3.1 Chemical etching

A mixture of HF and HNO_3 was adopted for chemically etching the Ti6Al4V flat plates and grid-like lattice structures (Fig 6.01.a & 6.01.b). HF readily reacts with Ti to form Ti hexafluoride complexes and hydrogen gas resulting in material removal, and in the case of lattice structures a reduction in strut size. Consequently, for the lattice structures, a slightly different grid design was required for each etching time-point (G0, G12 and G30) to ensure comparable strut diameter and pore size between groups (Fig 6.01.b). After etching, strut size was measured using optical microscopy (Fig 6.01.c). The strut diameter for G0, G12 and G30 groups were normally distributed, with mean values of 504, 499, and 498 μm respectively (Fig 6.01.d). The as-designed strut diameter and pore size are within the range considered suitable for osteointegration [222].

The design of the lattice is critical to controlling its functional properties [223], [224], [225]. Consequently, it is important to note that the grid like design is a simplification of the full lattice structure which is commonly implemented for biomedical applications [8], [9], [46], [213]. In order to study the cell behaviour in response to modifications in the surface alone, it is useful to minimise the effects of other factors which might influence the behaviour of the cell. However, for a lattice structure, a gradient in regulatory factors may develop within the implant. For example, the delivery of nutrients and oxygen inside the lattice may be less effective than to the periphery [226]. Such gradients are less likely to develop in the open cell grid design adopted here, and consequently may be more appropriate for the aims of this study.

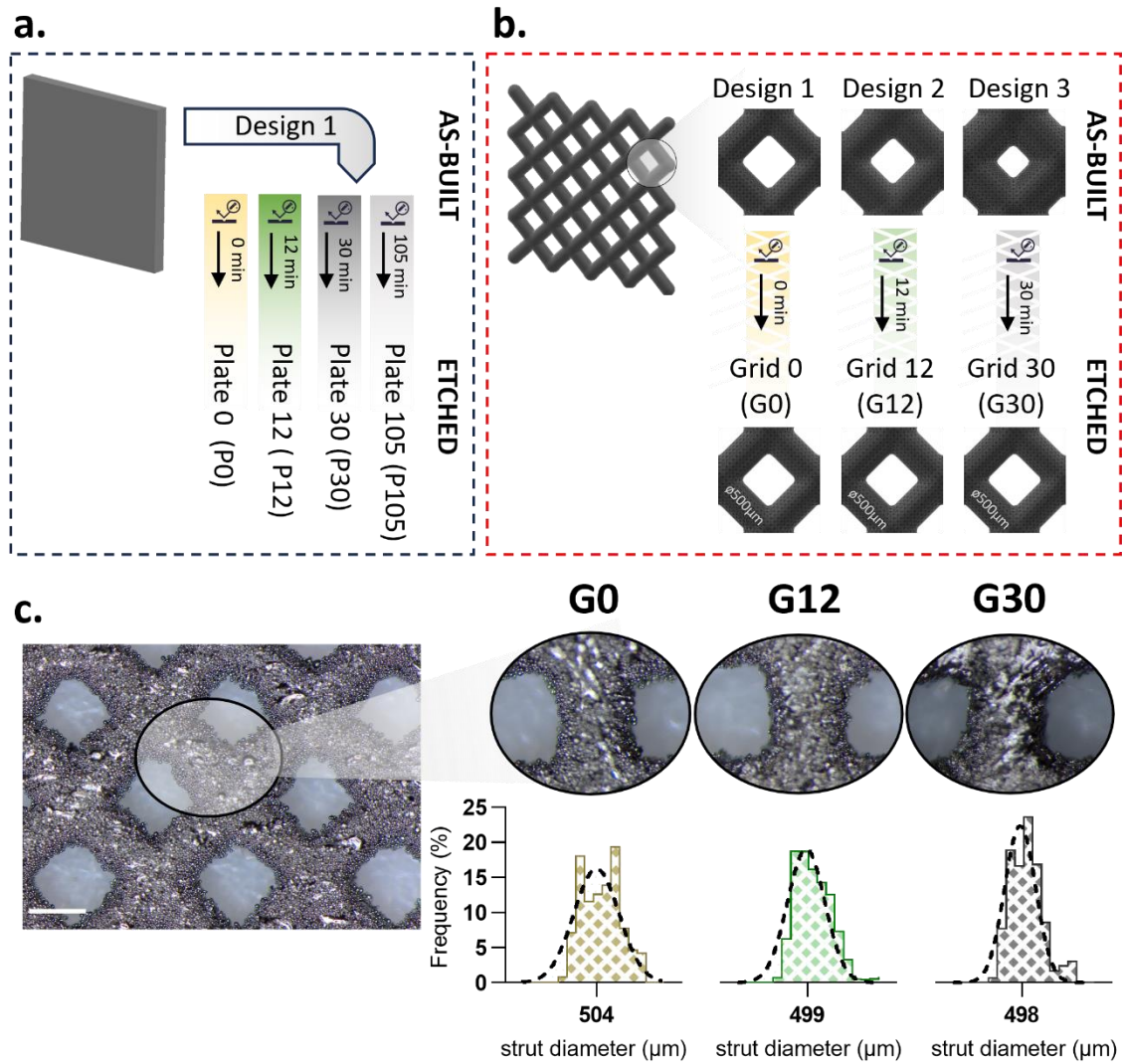


Figure 6.01. **Experimental design extended to (a) a simple flat plate geometry, and (b) a grid-like lattice.** Sub-groups were created accounting for the evolution of surface topology during the etching process. For a.) the plate geometry, one geometrical design could be used for all subgroups. For b.) the grid geometry, multiple geometrical design variations were required to ensure a consistent strut diameter after etching. c.) Strut diameter in each grid-like lattice group was assessed using optical microscopy. *All scale bars (white) are equal to 500 μm .*

The surface topology of as-built SLM fabricated components is a result of the aforementioned surface defects inherited from the fabrication process. Modifications in surface topology can be expected by the removal of these defects using chemical etching [140], [141], [190], [191], [227]. Here, we sought to assess the evolution of surface topology through a systematic etching process for a simple plate geometry, and a more complicated grid-like lattice structure.

From the SEM images, it is clear that the as-built surface topology of both the plate and grid groups is characterised by partially adhered powder (Fig 6.02). In addition to driving surface roughness and topology, these defects may also lead to a degradation of mechanical

properties. This is particularly notable in small diameter struts, as these defects account for a significant portion of the material volume [141]. In addition to these effects, partially adhered powder may also become dislodged *in vivo* if subjected to frictional forces, and subsequently pose a high risk to implant loosening and to an immunogenic response [228], [229].

On the flat plate, surface defects appear relatively homogenous across the geometry [65]. However, in the grid geometry, characteristic up-skin and down-down surfaces can be observed. Here, a rougher surface may arise on down-skin facing surfaces, as molten material more easily flows downwards by gravity and the capillary effect into voids in the underlying powder bed [65]. This also highlights the potential of other defects to arise as a result of geometry during SLM fabrication. For example, in triply periodic minimal surface (TPMS) lattice structures, powder may become trapped in the as-designed internal pores. This can occur alongside the aforementioned effects of partially adhered powder. Consequently, additional processing techniques such as ultrasonic vibration may be implemented in addition to chemical etching, as to minimise these effects [230]. However, trapped powder was not as much of an issue in this study due to the open cell grid structure that was implemented.

In both groups, chemical etching is successfully employed for the gradual removal of these defects. After the first time point, pitting can be observed, indicative of the corrosive attack of the etchant. By the final timepoint, the majority of remaining defects have been removed, revealing a relatively smooth surface. Despite this, discrepancies can be noted in the evolution of the surface between the two groups, with a slower etching rate apparent in the plate structures. This is evident in a higher frequency of defects remaining on the surface after the first and second time points. Additionally, a longer etching time is required to reach a smooth, defect-free surface. A number of studies have made comparable observations, and come to the conclusion that the effectiveness of the etching process is affected by geometry [141], [227].

We next sought to quantitatively reinforce these observations using WLI. In both geometries the side-skin surface was characterised. This acted as a more normalised location for assessment of the improvement in surface roughness throughout etching, compared to the up-skin or down-skin surfaces. Measurement of the up-skin or down-skin surfaces were also limited by the requirement of a line of sight using the WLI method. The S_a and S_z values changed as etching time was increased (Fig 6.02). In general, the surface roughness decreases up to the final etching time-point. However, an initial increase in S_a can also be observed for the plate geometry after the first time-point. This can be attributed to the slower etching rate. At this point, the same frequency of defects remain, however, their

surface roughness has increased due to the onset of pitting. After this point, the frequency of defects decreases, and surface roughness continues to decrease. At the final etching time-point, the inherent surface roughness of the bulk material becomes the dominant factor in determining the overall surface roughness. We have previously shown that there is little change in surface roughness beyond this point [141].

From SEM and WLI, it is also clear that topological non-homogeneities are primarily a consequence of partially adhered powder. Powder size was characterized using laser diffraction, noting a spherical morphology, with a nominal effective diameter between 24.5 μm (D10) and 55 μm (D90).

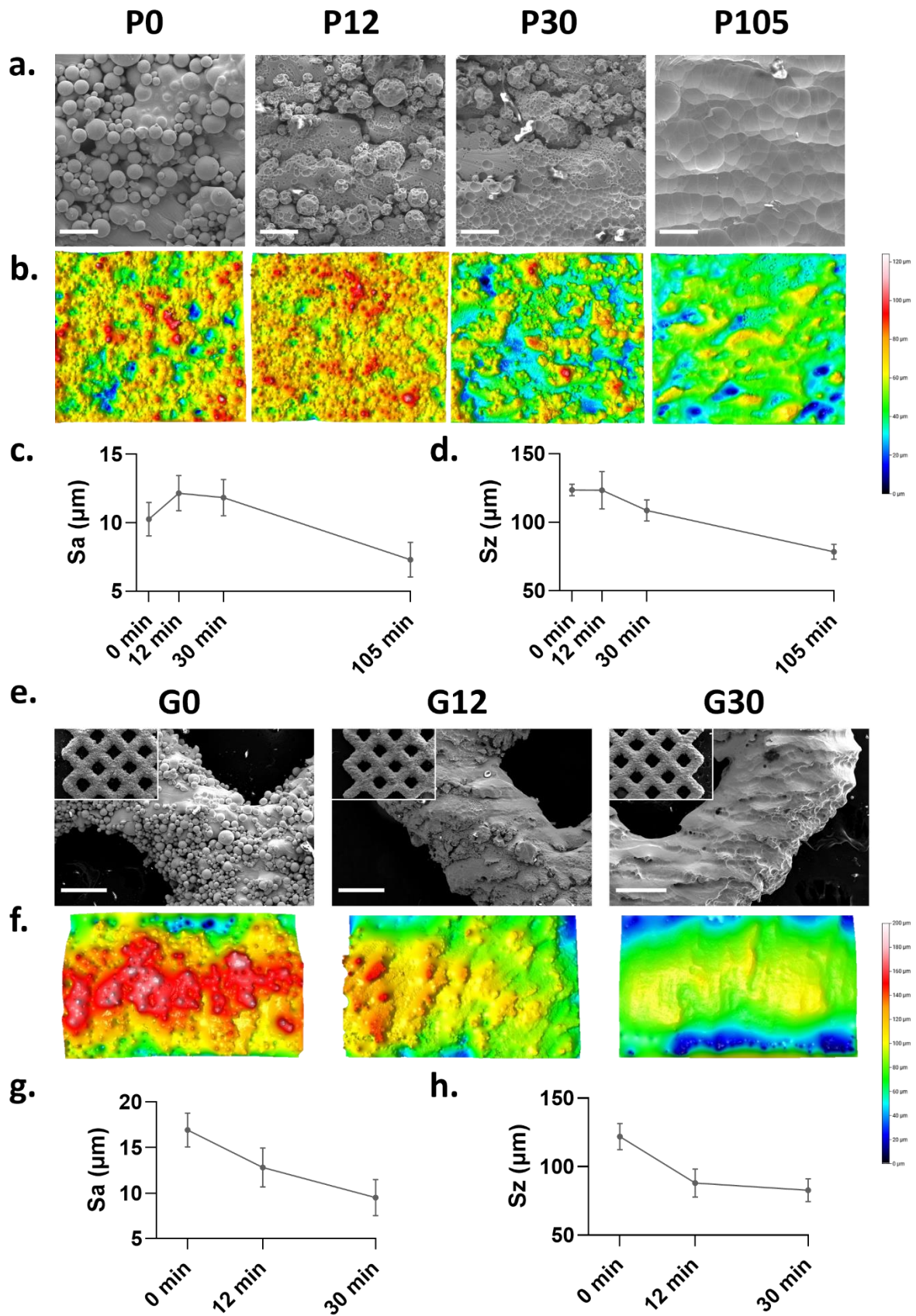


Figure 6.02. A spectrum of topologies were created by gradually refining the surface of SLM fabricated Ti-6Al-4V using an incremental HF/HNO₃ etching process. At each timepoint, surface topology was characterised using SEM and WLI analysis. a, e.) SEM micrographs and b, f.) WLI

reconstructions clearly show the gradual removal of surface inhomogeneities as etching time is increased. c, d, g, h.) The evolution of surface roughness is also quantitatively assessed from WLI S_a and S_z measurements ($n = 3$ samples, taken as the mean of 3 measurements). All error bars denote standard deviation. All scale bars (white) are equal to $250\mu\text{m}$.

6.3.2 Cellular viability and proliferation

In general, titanium is considered a biocompatible material and good cell viability has been observed on as-built and post-processed surfaces fabricated by SLM [115], [231]. However, varied results have been reported in regard to cell attachment and proliferation [232]. Here MSCs were directly seeded onto the metal surfaces to assess cellular viability, proliferation and osteogenic differentiation. Fluorescence imaging indicated MSCs were largely viable on day 1, with a larger number of viable cells observed at day 7, demonstrating cell proliferation on all material surfaces (Fig 6.03). Less cellular attachment was observed on the grid-like structures, which is likely due to their more complex geometry which negatively impacts the initial cell seeding. Despite this, extensive proliferation can be observed between day 1 and 7 across all constructs.

After chemical etching, it is critical that the residual etchant is adequately removed from the surfaces. As discussed in the methods section, samples were sonicated in isopropyl alcohol and deionized water. Given the low number of dead cells (Fig 6.03), it is likely that there is little or no remaining etchant on these surfaces.

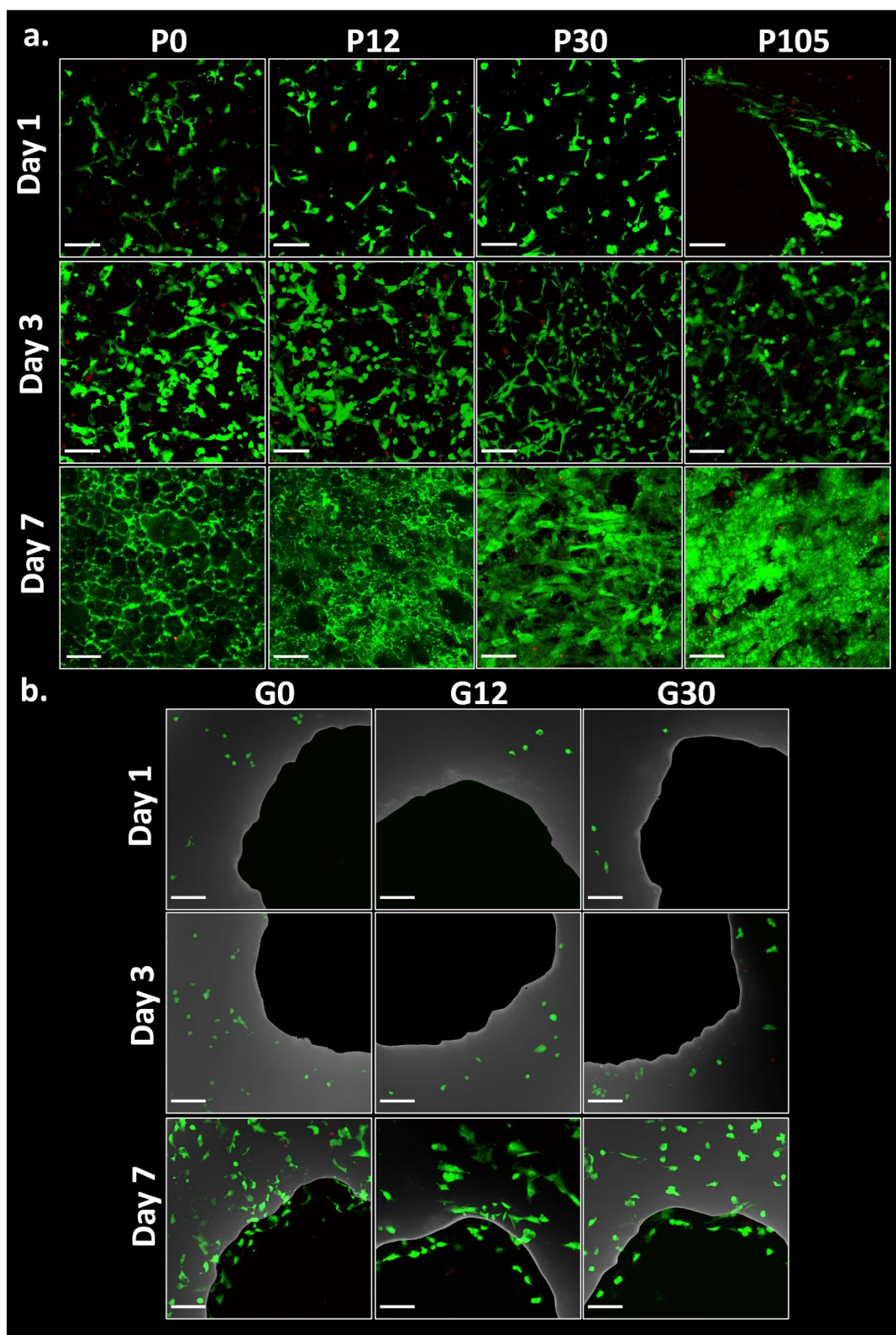


Figure 6.03. **All surfaces support high cell viability.** After etching, MSCs were seeded on the metal surfaces. Cell viability and proliferation was assessed on day 1, 3 and 7 for cells seeded on. a.) the flat plate groups, and b.) the grid groups. All scale bars (white) are equal to 100µm.

Cell proliferation was also quantitatively assessed by measuring changes in DNA content over 21 days of culture (Fig 6.04). There were no statistically significant differences observed as a function of surface type. However, a statistically significant increase in DNA content was observed between days 1 and 21 for all surface types. Cells continued to proliferate between days 7 and 21, therefore it is unclear if and when confluency is reached. Once cell density reaches a critical threshold, further cell division is typically constrained by contact inhibition [115], [233].

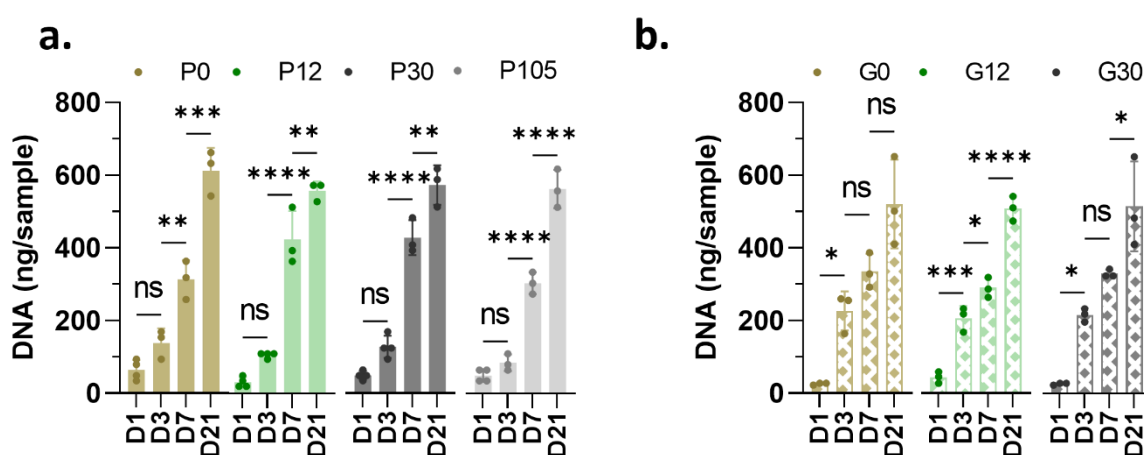


Figure 6.04. **All constructs exhibit extensive cell proliferation.** DNA Pico green measurements were used to assess cellular proliferation across Days 1, 3, 7, and 21 for cells seeded on a.) the flat plate groups, and b.) the grid groups. Extensive proliferation can be observed within each construct across this timeframe. All error bars denote standard deviation, *, **, ***, and **** indicate statistically significant differences (* $p < 0.0332$, ** $p < 0.0021$, *** $p < 0.0002$ and **** $p < 0.0002$, student's t -test). $n = 3$ samples, taken as the mean of 3 measurements.

6.3.3 Cellular morphology and organization

Cell morphology, including cell spreading and elongation, has been shown to regulate osteogenic differentiation of MSCs. Changes in morphology act as a biophysical cue for the activation of mechanosensitive signalling pathways, with consequential regulation of gene transcription to control cellular functions and phenotypes [113], [114].

In this work, changes in cellular morphology and organisation were assessed using SEM (Fig 6.05). In general, early cell-substrate interactions are characterised by passive adhesion, and spreading from the typically spherical morphology in suspension. This is followed by a more active phase of reorganisation, characterised by the formation of focal adhesion complexes, which transduce continuous mechanosensitive remodelling [112],

[234]. Here, extensive cell spreading could be observed across all experimental groups. This was apparent by day 1, with the majority of cells beginning to flatten and spread. This is also associated with MSC differentiation along an osteogenic lineage (towards osteoblasts), having been shown to increase intracellular tension, with subsequent activation of osteoinductive signalling pathways [32].

It is also clear that cell morphology is largely influenced by local topological features. Independent of overall roughness, feature size and patterning can direct cell migration by contact guidance. This largely occurs as a response to avoid high energy discontinuities across topological inhomogeneities [235], [236]. Previous studies have shown better cell alignment on features the same order of magnitude as their own size [237], [238]. In this work, we have shown that the as-built surface is characterised by a high frequency of spherical particles, spanning a magnitude close to that of a typical MSC. From SEM, we can also note that cell spreading on the as-built 'Go' surface appears to be directed by these local topological features. It is well understood that surface energy is an important regulator of cellular attachment and spreading [239], [240]. Higher surface energies have been associated with higher roughness and consequently, the as-built surface may likely impede initial wetting [240]. As discussed in the following paragraphs, subsequent cell spreading may adapt in order to minimise contact with high energy discontinuities [237], [238].

By day 1 of culture, cells have developed a stretched, anisotropic morphology. Cells appear anchored to the powder, and are often accompanied by a distinct trailing edge. Similar behaviour has been observed in the literature, and attributed to filopodia sensing, and subsequently, lamellipodium (a cytoskeletal actin projection on the leading edge of the cell) forming a stable anchor by wrapping around the spherical geometry [220], [241]. In addition, previous studies have demonstrated that similar anisotropic spreading may impede mechanotransductive cytoskeletal stressing required for nuclear signalling and subsequent osteogenic differentiation [242].

By day 7, cell spreading appears more isotropic on the as-built 'Go' surface. No obvious sign of a trailing edge is visible, and anchoring appears more homogenous around the titanium powder. Cells are continuing to spread, as indicated by the filopodia protrusions bridging the gap between adjacent powder particles. Consequently, large areas of the cell are unsupported, bridging gaps across the non-homogeneous powder interface. Similar behaviour on micro-patterned surfaces has been attributed to contact guidance effects [238], [243], [244]. The lack of basolateral support across these non-adhesive gaps has been associated with low intracellular tension, and reduced osteogenic potential [244].

As etching time is increased, the frequency of surface defects is reduced. Consequently, cell spreading appears more isotropic and is increasingly supported at the cell-substrate interface. MSC differentiation towards an osteoblastic lineage is usually accompanied by similar basolateral isotropic spreading [242]. This behaviour is apparent for the majority of cells through days 1 to 7. However, a distinct second morphology can also be observed in a small number of cells in the G30 group by day 7. Their morphology can be characterised by a stellate shape with numerous dendritic protrusions, and observed in the vicinity of fibrous matrix. This is consistent with the change in morphology observed for osteoblast maturation typically associated with entrapment in the newly formed unmineralized bone matrix [34], [37].

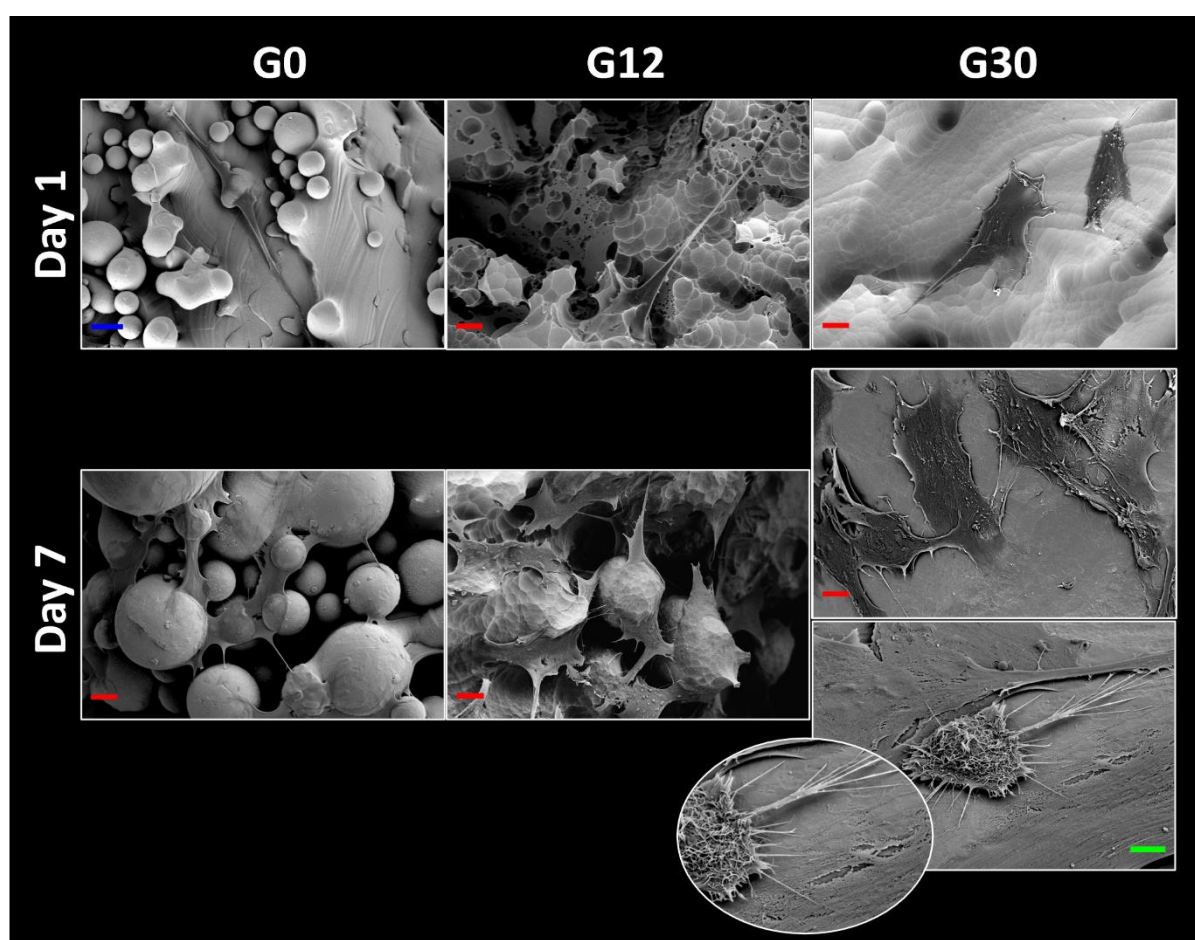


Figure 6.05. Cell morphology is influenced by local topological features. After seeding on the grid constructs, cellular morphology and organisation was assessed using SEM across days 1 and 7. It is clear that refinement of the as-built surface using chemical etching has an extensive effect cell spreading. Similar to confocal observations, it appears that cell spreading is guided by surface inhomogeneities such as partially adhered powder. As defects are gradually removed via etching, cell spreading appears more homogeneous. Scale bars are equal to 20 μ m (blue), to 10 μ m (red) and to 5 μ m (green).

Confocal imaging reinforced SEM observations (Fig 6.06). Similarly, extensive cell spreading can be observed across all experimental groups. As indicated by f-actin

configuration, the majority of cells are beginning to spread and flatten by day 1. On the as-built surface (Po), it appears that cells are being arranged around local topological features. As this is consistent with that observed under SEM, it is clear that these features are most likely partially adhered titanium powder. This behaviour can also be observed in subsequent etching time points, however in general, spreading appears more isotropic as etching time is increased. This can be attributed to the gradual removal of surface defects and inhomogeneities with increased etching time.

As we have discussed, early cell-substrate interactions are characterised by passive spreading, which has been described as akin to the manner in which liquid initially adheres to a surface. This phase of cell-surface interaction is followed by the formation of focal adhesion complexes, which bridge the gap between the substrate and actin cytoskeleton [112], [234]. These adhesions exhibit continuous mechanosensitive remodelling, exerting extensional and contractile forces on the actin fibres, reinforcing cell spreading [112], [114], [234], [245]. Consequently, focal adhesions serve as indicators of cell-surface interaction, and cell response can be studied by following the recruitment of focal adhesion proteins such as vinculin. Here, vinculin suggested a similar expression of contact points across all surfaces, indicating firm cell-substrate contact (Fig 6.06).

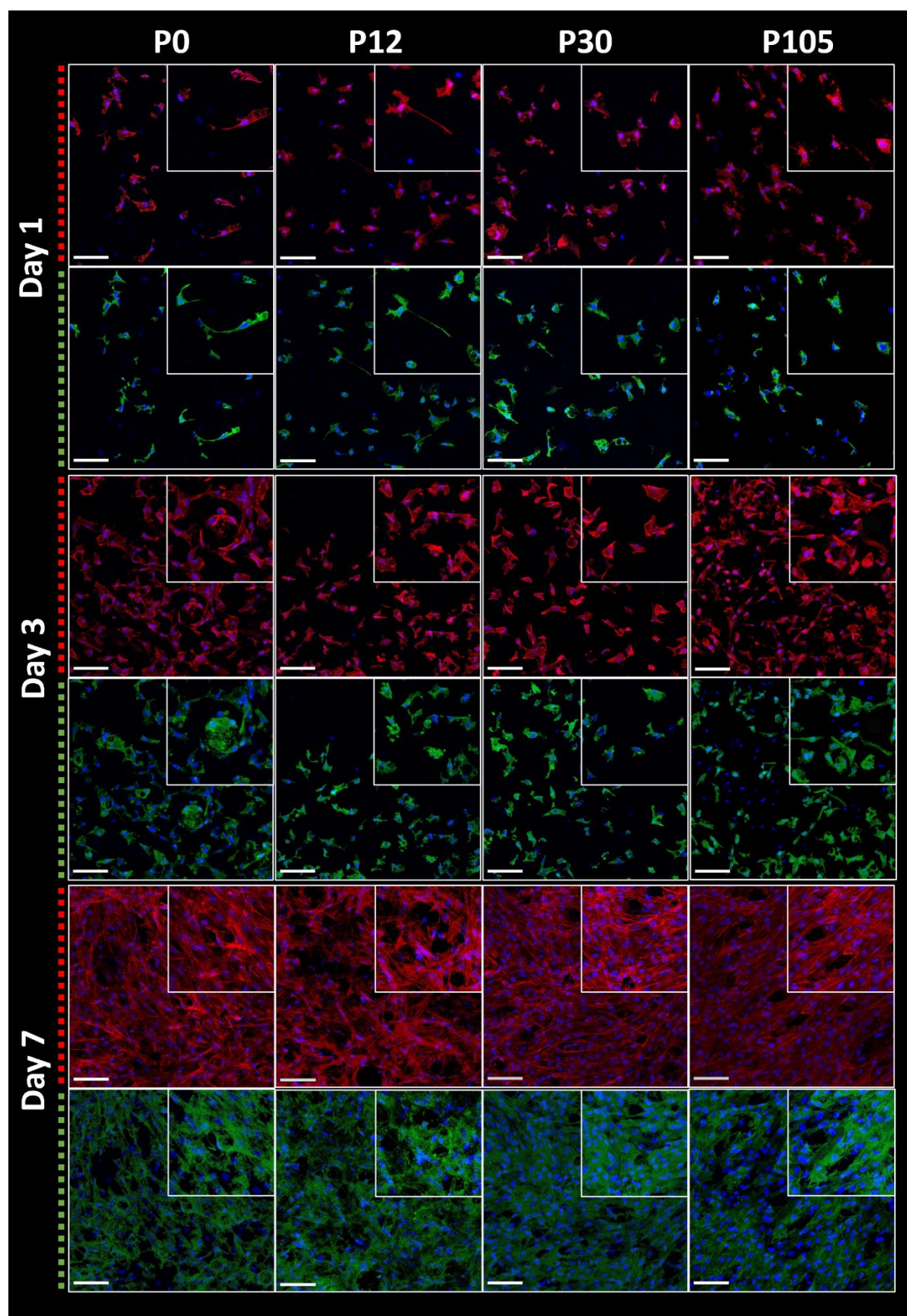


Figure 6.06. **Confocal imaging of MSCs on the surface of the plate constructs.** Confocal imaging was used to assess the development of cellular morphology and organisation across days 1, 3 and 7, after

seeding on the flat plate constructs, with staining for cell nuclei (blue), f-actin (red) and vinculin (green). All scale bars (white) are equal to 250µm.

Although not a primary focus of this study, pore size plays a critical role in the osteointegration of porous biomedical implants. In general, pores must be large enough to allow cell migration and capillary formation. However, pores that are too large can bring about their own problems, including insufficient mechanical properties and slow proliferation [222]. For additively manufactured Ti64, a pore size in the range of 200-700µm is widely considered suitable for osteointegration [222]. In this study, a 500µm² pore size was targeted. From confocal imaging, it is clear that by day 21, cells have adequately bridged the pores and are homogenously spread across the scaffold (Fig 6.07).

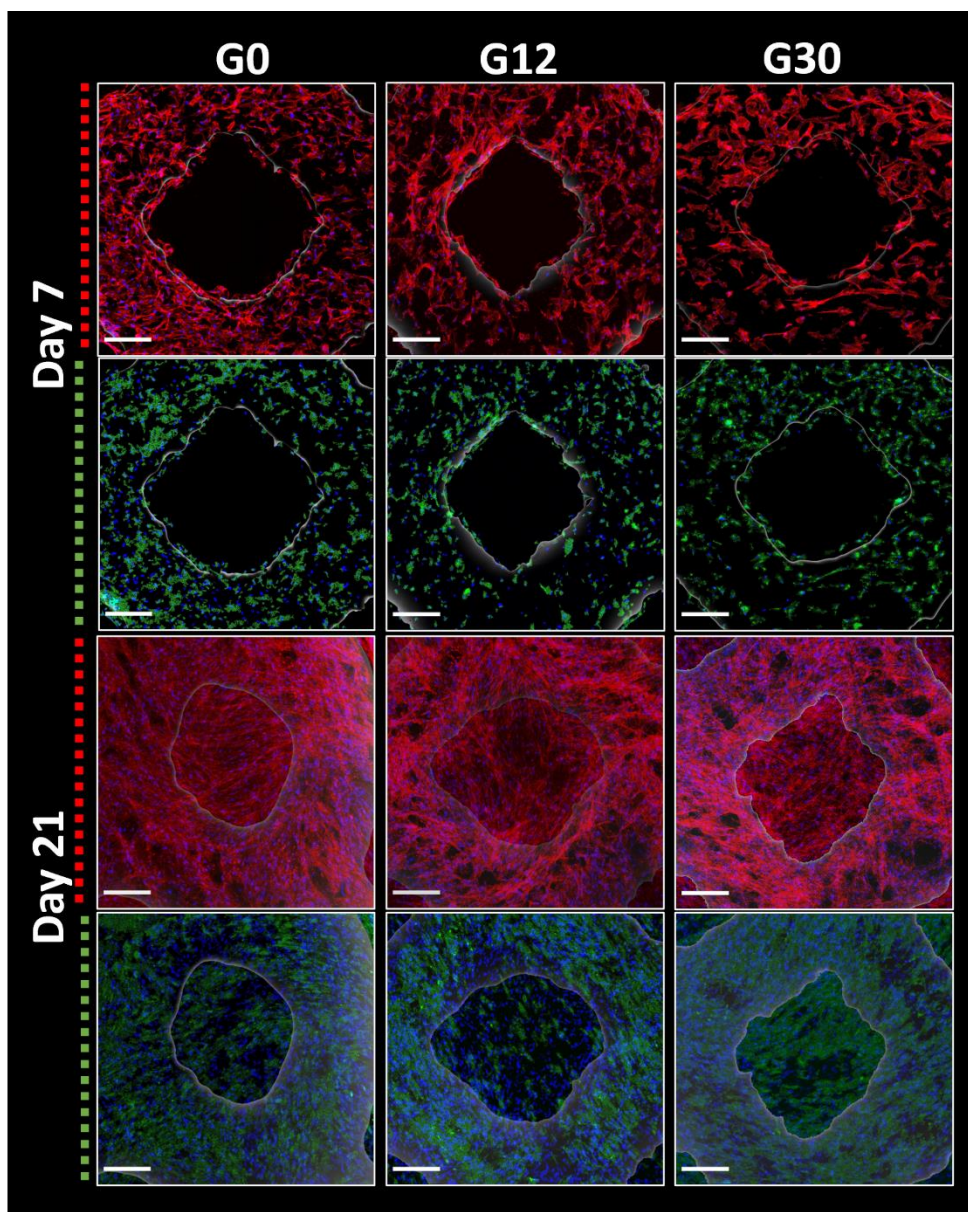


Figure 6.07. **Cells have adequately bridged pores and are homogenously spread across the grid constructs.** Confocal imaging was used to assess the development of cellular morphology and organisation

across days 7 and 21, after seeding on the grid constructs. This was extended to cell nuclei (blue), f-actin (red) and vinculin (green). By day 21, cells have completely bridged the pores and are homogeneously spread across each surface. All scale bars (white) are equal to 250µm.

6.3.4 MSC osteogenesis on etched surfaces

We next assessed the expression of genes associated with MSC osteogenesis and the activation of mechanosensitive signalling pathways for cells seeded on the different metal surfaces (Fig 6.08). Focal adhesions play a central role in mediating cell-substrate adhesion. Cadherin 11 (CDH11) and focal adhesion kinase (FAK) were identified as potential targets associated with this process. CDH11 is part of the cadherin family of transmembrane proteins that play a critical role in cell-cell adhesion [246], [247], [248]. CDH11 is distinct from other cadherins in that it can dually interact with the substrate by binding with syndecan-4, and participate in focal adhesion related signalling pathways [247], [248]. FAK, a signalling protein involved in early cell-substrate interactions, is recruited to focal adhesions by integrin activity, and activated through autophosphorylation [25], [112], [114]. It is an initial step to activate further mechanosensitive signalling cascades [25]. Despite differences in surface topology, no obvious trends could be observed in CDH11 or FAK expression across the experimental groups (Fig 6.08). This was perhaps unsurprising given the expression of vinculin, which suggested comparable development of focal adhesion contact points across all surfaces (Fig 6.07 and Fig 6.08).

Similarly, runt related transcription factor 2 (RUNX2), Osteopontin (SPP1), and Bone Sialoprotein (IBSP) were identified as potential targets associated with osteogenic differentiation. RUNX2 is a transcription factor involved in early osteogenic differentiation, and associated with commitment of MSCs towards an osteoblast lineage [32], [33], [35]. Its level peaks in immature osteoblasts, having activated the expression of osteogenic markers, including SPP1 and IBSP [35], [249]. Subsequently, SPP1 and IBSP are associated with later stage differentiation. While some trends towards increased gene expression was observed on the P105 substrate at day 21, no significant differences were observed in RUNX2, SPP1 or IBSP expression across the experimental groups (Fig 6.08). However, PCR analysis is merely a snapshot in time, and it is possible our time points did not align with the upregulation of these genes.

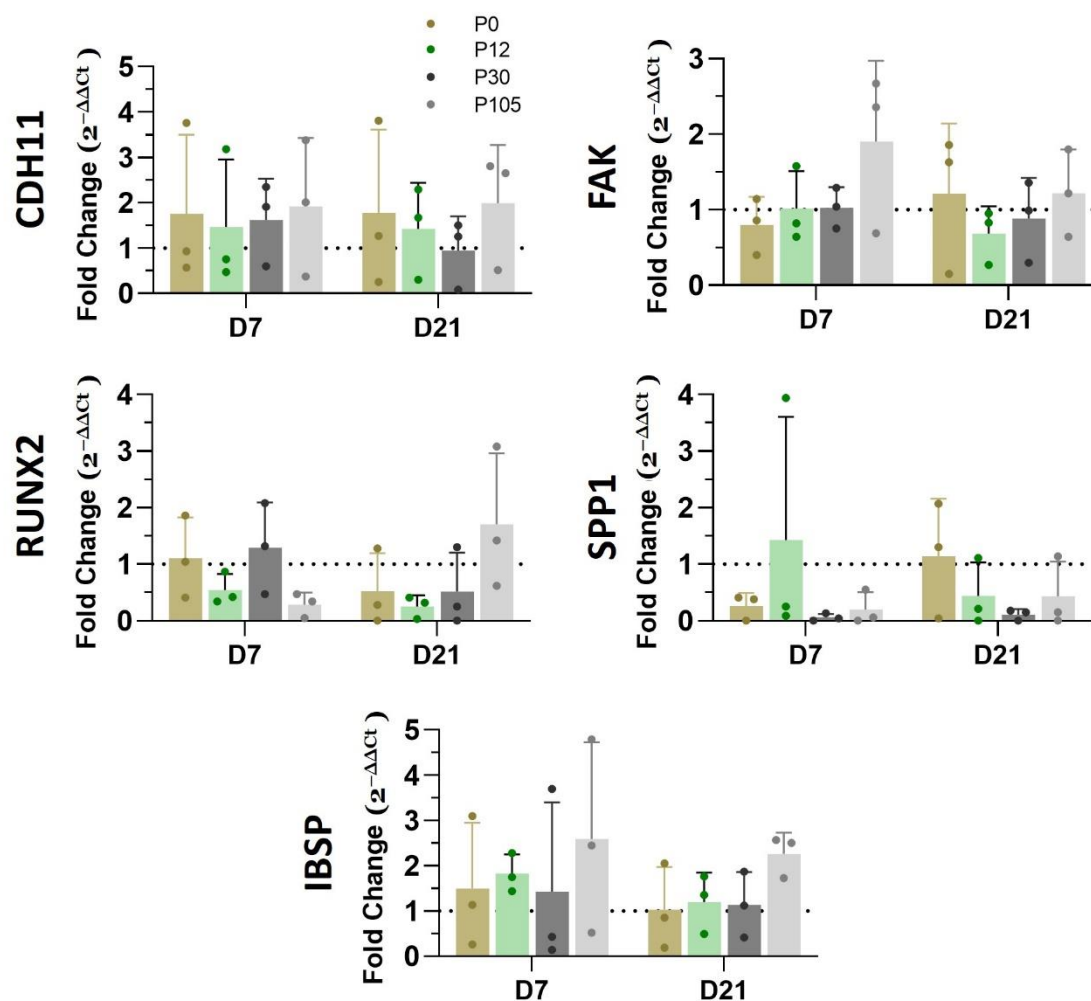


Figure 6.08. **Gene Expression.** Cadherin 11 (CDH11) and focal adhesion kinase (FAK) were identified as potential targets associated with adhesion, and runt related-transcription factor 2 (RUNX2), Osteopontin (SPP1), and Bone Sialoprotein (IBSP) with osteogenic differentiation. Data is reported in fold change relative to the control group. All error bars denote standard deviation. $n = 3$ samples, taken as the mean of 3 measurements.

Despite no significant differences in mRNA expression, we finally sought to examine if changes to the metal surface would impact mineralisation. Osteoblasts are primarily responsible for the active development of new bone [32], [33], [34], [35]. During early maturation, they begin to secrete osteoid, an unmineralized organic matrix primarily comprised of collagen type 1 and non-collagenous proteins [32], [35]. Following this, matrix mineralisation occurs in the osteoid through growth of hydroxyapatite nanocrystals; derived from calcium and phosphate ion concentrations [33]. In this work, mineralised matrix deposition was assessed *via* Alizarin Red staining marking the deposition of calcium. Positive staining can be observed across all groups, but is clearly more pronounced as etching time is increased, indicating more extensive mineralisation on the P105 and G30 samples (Fig 6.09.a & 6.09.b). EDX elemental microanalysis also

confirmed the presence of calcium and phosphorous peaks in the most extensively stained samples (Fig 6.09.c).

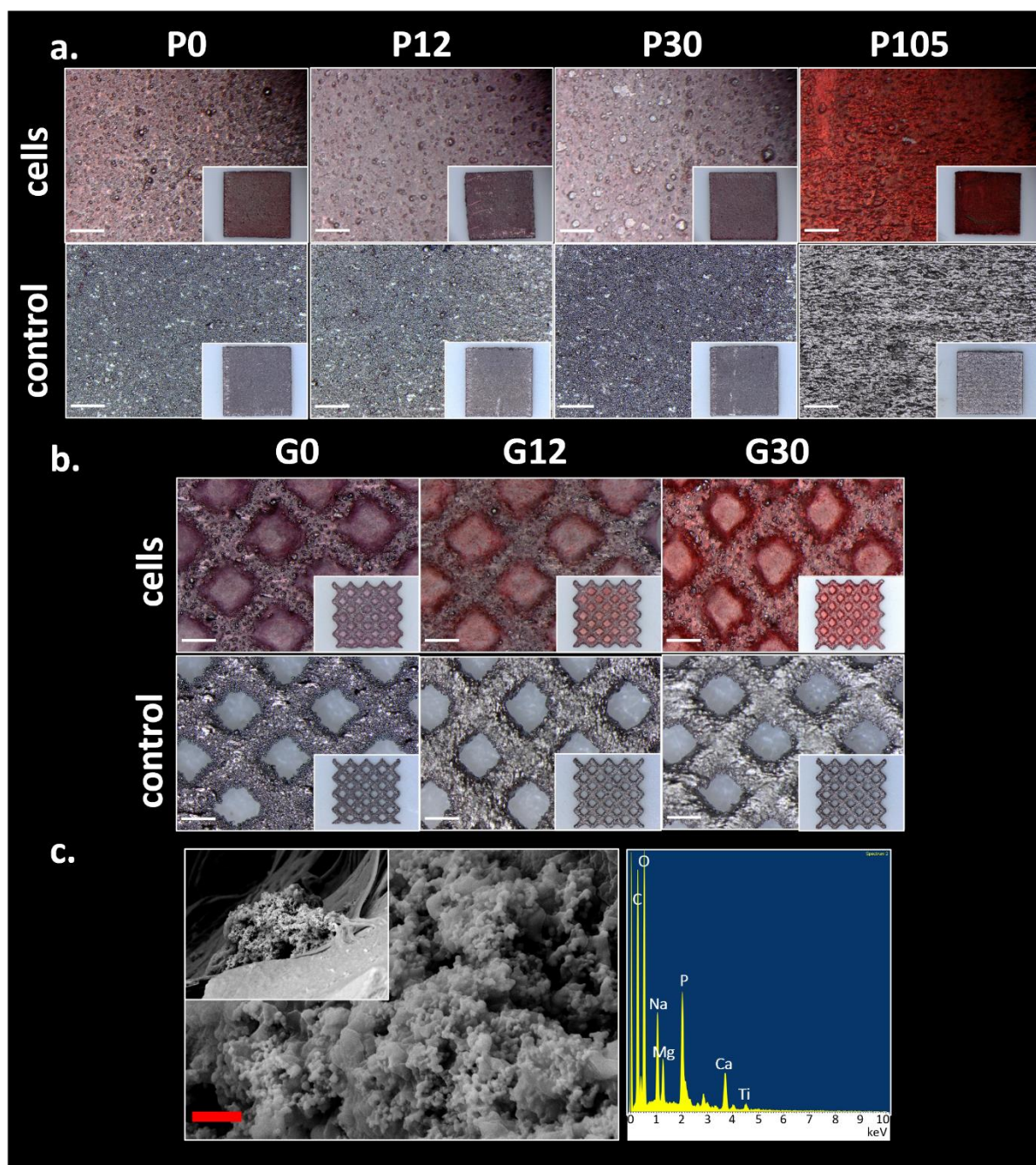


Figure 6.09. Mineralisation is more extensive as etching time is increased. Mineralisation was assessed on day 21 via Alizarin red staining marking the deposition of calcium. Positive staining can be observed across all groups, but was clearly more pronounced as etching time is increased. This trend is evident across both a.) the flat plate, and b.) the grid constructs. Mineralisation was confirmed using SEM-EDX analysis on the G30 grid construct. c.) Mineralised matrix is confirmed showing the presence of Calcium (Ca) and Phosphate (P) EDX peaks. Scale bars are equal to 500µm (white) and 10µm (red).

6.4 Conclusion

In this work, MSCs were directly seeded onto additively manufactured Ti-6Al-4V surfaces. The potential benefits of treating these surfaces with post-process chemical etching in a solution of HF and HNO₃ was investigated. We found that by using an incremental etching process, surface defects could be gradually removed from the as-built surface, allowing cell-substrate interactions to be studied across a spectrum. As these defects were gradually removed, cells remained viable, and extensive proliferation could be observed across all surfaces through the 21 days of culture. Cell morphology was clearly influenced by local topological features. Topological non-homogeneities on the as-built surface, such as partially adhered powder, drove a stretched, anisotropic morphology. Continued spreading across the non-homogeneous powder interface resulted in large areas of the cell being unsupported as they bridged gaps across the material surface. As the etching process was continued, surface defects were gradually removed and cell morphology appeared more isotropic, which is generally supportive of MSC differentiation along an osteoblastic lineage. By day 21, increased mineralisation could be observed on the most extensively etched surfaces, indicative of progression along an osteogenic pathway. These findings point to the benefit of post-process chemical etching of additively manufactured Ti-6Al-4V biomaterials targeting orthopaedic applications.

Chapter 7: Conclusions and future work

7.1 Conclusions

In this work, we examined the manufacturability of micro-strut lattice structures, fabricated through PBF. Adopting standardized micro-strut dog-bone geometries, we were able to isolate geometrical variations between different lattice designs, and study the bulk properties of the material as a function of strut diameter. Using this approach, we investigated the inheritance of defects and microstructural characteristics in micro-strut lattices, as well as their effect on mechanical and biological properties.

In Chapter 3, we examined the inheritance of porous defects in micro-lattices fabricated through PBF. In this work, we found that a high frequency of porous defects were inherited in small diameter struts, for a set of printing parameters that had yielded optimal density in bulk sized components. This could be correlated to higher rates of heat loss in the small diameter struts, on account of their high surface-to-volume ratio. Consequently, a higher energy density input was required for processing micro-strut lattices, with a similar level of density to that achieved in bulk sized components. Minimization of these defects coincided with improved quasi-static mechanical properties. Improvements in strength and stiffness were credited to an increase in the percentage volume of load bearing material, while improvements in failure strain was largely attributed to the minimisation of stress concentrations surrounding the irregular pore morphologies. On the contrary, porous defects did not significantly impede the fatigue properties beyond the effect of yielding. During fatigue loading, cracks generally initiated from surface defects, even in the presence of large internal pores. This could be credited to an increased surface free energy, and highlights that other process inherited defects may remain an issue, after optimizing material density.

Having optimized material density, in Chapter 4 we sought to investigate the effects of other process inherited factors, which may also affect the mechanical properties of small diameter struts. This was extended to the uptake of surface defects, as well as changes in microstructure, across different strut diameters. In this work, we found that surface defects represent a significant percentage of the total material volume of micro-struts. This resulted in a decrease in the amount of material that is load bearing in any given cross-section, and consequently led to an apparent decrease in stiffness, and a reduced resistance to plasticity. Furthermore, as surface defects account for an increasing percentage of the total material volume as strut diameter is decreased, these effects contribute to a degradation of mechanical properties in smaller diameter struts. By normalizing

mechanical properties to the core load-bearing area, we were able to isolate these effects and study the contribution of other process inherited factors toward mechanical properties. After normalization of this data, an increase in stiffness, and a reduction in strain to failure in the smaller diameter struts could be correlated to microstructural characteristics. Due to the strong texture towards $\langle 0001 \rangle$, the increase in stiffness correlated with lower angles between the relatively stiff c-axes and the global loading direction. Similarly, favourable orientation towards low energy slip systems and high texture, correlated with a lower strain to failure and a more brittle cleavage-like fracture. Despite these effects, changes in microstructure and strut morphology between the different strut diameters did not lead to any significant changes in fatigue properties beyond the effects of yielding. Due to low fracture toughness, the fatigue resistance of titanium alloys is largely dictated by resistance to crack initiation. Across the different strut diameters, the critical site of crack initiation could be rooted in stress concentrations around surface defects, highlighting their detrimental impact on fatigue properties, in addition to reducing the load bearing capacity.

Given the detrimental impact of surface defects on the quasi-static and fatigue mechanical properties of micro-struts and lattices, we next sought to implement post-processing techniques for refinement of the as-built surface. In Chapter 5, we implemented chemical etching as a means of post-process surface cleaning. Using this approach, we were able to successfully refine the as-built surface of additively manufactured lattice structures, circumventing issues around the requirement of a line of sight with traditional techniques such as grinding or polishing. By extending this process to etch the micro-strut dog-bone geometries, the resulting improvement in mechanical properties could be characterised alongside the gradual removal of surface defects. Following etching, an improvement in the quasi-static mechanical properties could be credited to the minimisation of non-load bearing material. In fatigue, crack initiation could still be rooted in surface and near-surface defects. However, a reduction in surface roughness led to an improved resistance to HCF, which is largely dictated by resistance to crack initiation.

Modification of the implant surface is also likely to play an important role in mediating cell behaviour. In addition to mechanical properties, the overall success of orthopaedic implants is largely driven by cellular responses at the implant surface. Therefore, in Chapter 6, we sought to examine the influence of chemical etching on cell-substrate interactions. Using an incremental etching process, surface defects were gradually removed from the as-built surface, which allowed the response of MSCs to be studied across a spectrum of topologies. As surface defects were gradually removed, cells remained viable, and extensive proliferation could be observed through 21 days of culture. On the

other hand, an increase in mineralization could be observed on the most extensively etched surfaces, indicative of MSC differentiation further along an osteogenic pathway. This could be correlated to the changes in cell morphology, which occurred in response to the different surface topologies achieved through etching. On the as-built surface, cell morphology appeared to be influenced by local topological features, such as partially adhered powder. Early cell spreading on this surface could be characterized by migration onto these features, resulting in a stretched, anisotropic morphology, correlated with reduced osteogenic potential. At a later stage, cells appeared more homogeneously anchored around the titanium powder. However, continued spreading was also indicated by filopodia protrusions, and resulted in large areas of the cell suspended across the non-homogeneous powder interface; an attribute leading to a lack of basolateral support, correlated with low intracellular tension, and reduced osteogenic potential. After continued etching, surface defects were gradually removed, revealing a much more homogeneous surface. Through the 21 days of culture, this was accompanied by basolateral isotropic cell spreading, similar to that of MSC differentiation towards an osteoblastic lineage.

7.2 Closing Remarks

In summary of this work, we have investigated the manufacturability of micro-strut lattices fabricated through powder bed fusion. We have demonstrated that process inherited defects and characteristics have a significant impact on the mechanical and biological properties of small diameter struts. By optimization of in-process parameters, and adoption of post-processing techniques, the majority of these defects could be minimised, and resulted in significant improvements in the quasi-static and fatigue mechanical properties, as well as cell-substrate interactions when applied to biomedical implants.

7.3 Suggestions for future work

7.3.1 The evolution of microstructure as a function of strut diameter

In Chapters 3 and 4, we investigated the uptake of a number of process inherited factors in micro-lattices. This was extended to microstructure. Microstructural features were measured at the centre of the micro-strut gauge section of each group. Here, changes in grain size and texture could be correlated to strut diameter. Consequently, this could be correlated to the cooling rate, differentiated between the different strut diameters by changes in the surface-to-volume ratio. Although these localized scans gave us a picture of the microstructural trends between the different strut diameters, it was only a snapshot. Microstructure most likely also changes across the cross-section of each strut. This might

be captured using larger EBSD scans, and result in a much more fundamental insight into the evolution of microstructure as a function of strut diameter. As the α' martensite phase nucleates from the prior- β grain boundaries, a critical part of this work would be the reconstruction of the prior- β grains. This was not possible in our work, due to the small size of the scans that were acquired. However, the evolution of the β phase is dependent on thermal gradients during solidification, and consequently may be influenced by discrepancies in the thermal gradient across the cross-section of a strut. Therefore, the prior- β grain boundaries are a critical feature that should be captured in order to understand the effects of strut diameter on microstructure. On further cooling, the β -phase transforms into α/α' [123]. Although there are a large number of α/α' variants that may precipitate from the prior- β grain boundaries, the final microstructure of α/α' phase is strongly influenced by the prior- β phase [123]. This process is further complicated by the remelting of the material within, and between layers. This includes the remelting of material by parallel scanning tracks in the C&H printing strategy. Consequently, other printing strategies may be more suitable for understanding the relationship between microstructure and strut diameter. The single-point approach is a much simpler strategy, and does not involve remelting of material within each layer [50]. In this approach, each slice of the CAD geometry is assigned a single vector point (Fig 7.1). The laser continually scans this point, increasing the size of the melt pool, and subsequently, strut diameter. By isolating the effects of remelting within each layer, this approach may be more suitable for studying which factors might drive differences in microstructure between different strut diameters.

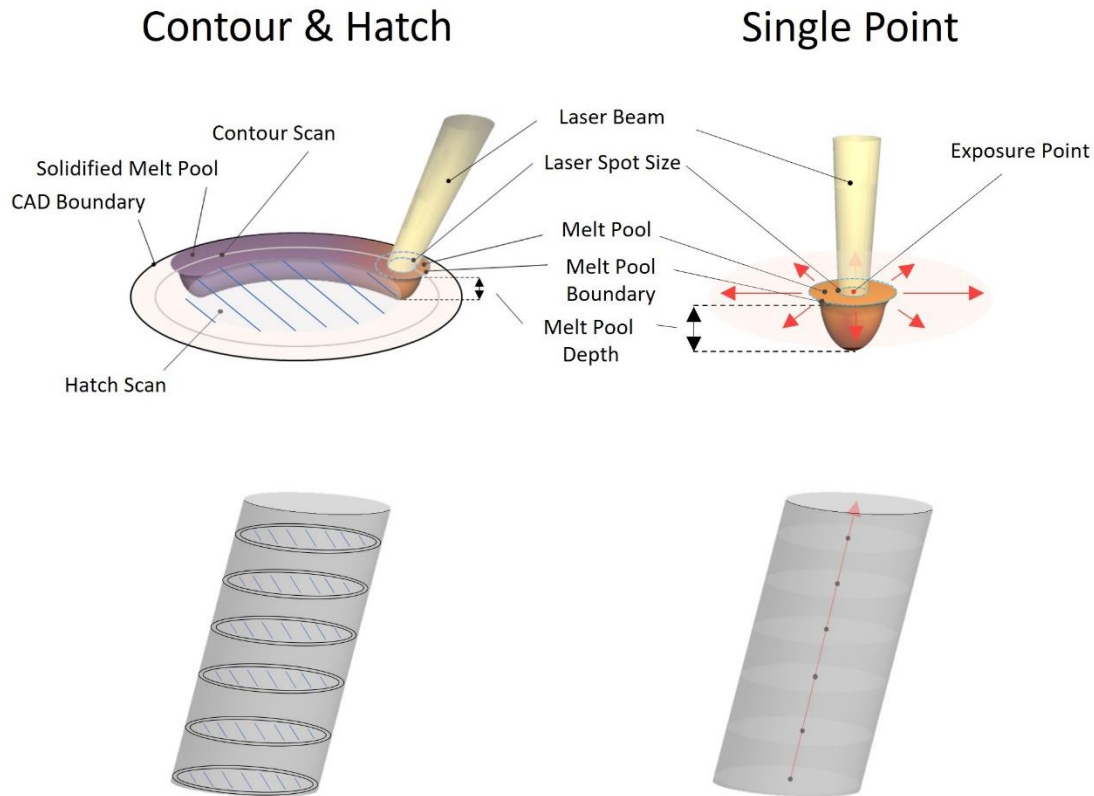


*Figure 7.1. **PBF printing strategies.** A contour-and-hatch scanning strategy or a single-point strategy can be implemented in PBF fabrication. In the C&H approach, each layer of the CAD geometry is processed by an outer contour scan and the enclosed area is then processed by inner hatch scans. In the single-point approach, each slice of the CAD geometry is assigned a single vector point, onto which the laser is continually scanned, increasing the size of the melt-pool, and subsequently strut thickness.*

7.3.2 Minimizing microstructural differences between different strut diameters using heat treatment

In Chapters 3 and 4, we identified a number of process inherited characteristics that lead to a degradation of mechanical properties in micro-strut lattices. This included the inheritance of surface defects, and microstructural characteristics. Fortunately, the effects of surface defects could be alleviated using post-process chemical etching, as described in Chapter 5. However, differences in microstructure between the different strut diameters were not addressed. These effects might be minimized using a suitable post process annealing step. In this approach, the final rate of cooling might be controlled, as to account for faster cooling rates in smaller diameter struts.

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