X-ray imaging of powder consolidation
during laser additive manufacturing

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### Nomenclature (I)

**Roman alphabet**

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<th>Description</th>
<th>Unit</th>
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<tr>
<td>$A$</td>
<td>Laser absorptivity</td>
<td>-</td>
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<td>$A_N$</td>
<td>Andrew number</td>
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<tr>
<td>$d$</td>
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<td>mm</td>
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<tr>
<td>$d_{point}$</td>
<td>Point distance (PD)</td>
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<tr>
<td>$G$</td>
<td>Thermal gradient</td>
<td>K/m</td>
</tr>
<tr>
<td>$h$</td>
<td>Hatch spacing</td>
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<tr>
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</tr>
<tr>
<td>$l$</td>
<td>Length of the molten pool</td>
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</tr>
<tr>
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<td>Laser power</td>
<td>W</td>
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<tr>
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<tr>
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### Nomenclature (II)

#### Greek alphabet

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<td>The angle between the directions of the moving laser beam and crystal growth</td>
<td>°</td>
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<td>(\alpha_{\text{thermal}})</td>
<td>The thermal diffusivity of a material</td>
<td>m(^2)/s</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>Surface tension</td>
<td>mN/m</td>
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<tr>
<td>(\Delta T)</td>
<td>The temperature difference between maximum temperature of the molten pool and the solidus temperature of the material</td>
<td>K</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Cooling rate</td>
<td>K/s</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Efficiency of the laser-matter interaction</td>
<td>-</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength</td>
<td>nm</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Dynamic viscosity</td>
<td>Pa. s</td>
</tr>
<tr>
<td>(\mu_{\text{coeff}})</td>
<td>The linear attenuation of coefficient</td>
<td>1/m</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density</td>
<td>Kg/m(^3)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>The wetting angle between the substrate and molten pool</td>
<td>°</td>
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Abstract

The laser-matter interaction and powder consolidation in laser additive manufacturing (LAM) occur on very short time scales ($10^{-6} - 10^{-3}$ s); and they have proven difficult to characterise. A better understanding of the underlying mechanisms during LAM is crucial for prediction and optimisation of part properties. This thesis highlights the development and applications of a LAM process replicator (LAMPR), combined with in operando high-speed synchrotron X-ray imaging and image analysis to study these mechanisms. Using this setup, the sequential powder consolidation phenomena were revealed in LAM of stainless steel (SS316L), a Fe-Ni alloy (Invar36) and bioactive glass (13-93).

The consolidation mechanisms of alloy powders are driven by molten pool wetting and vapour-driven powder entrainment. The principal consolidation mechanism of 13-93 bioactive glass is driven by viscous flow. The evolution of porosity and spatter were revealed during LAM of virgin and oxidised Invar 36 powders under different build conditions. The oxide films altered the Marangoni convection from centrifugal to centripetal, restricted the melt flow (and gas transport) in the melt track and promoted pore growth. Several new pore mechanisms were uncovered, including pore migration, dissolution, dispersion, and bursting. The laser-induced gas/vapour jet promoted the formation of melt tracks and denuded zones while ejecting spatter at velocities up to 1 m/s along the argon gas flow and laser scanning directions. In addition, a new spatter mechanism has been discovered; spatter can be formed by laser-driven gas expansion. Laser re-melting of large pre-existing pores can result in two extreme outcomes: (1) pore healing by Marangoni flow and (2) formation of droplet spatter and open pore. These results have clarified the physics behind previous hypotheses and proposed new mechanisms in LAM, which are critical for the development of LAM and simulation models of the process.
Declaration

I hereby certify that the work presented in this thesis is the result of my own investigations carried out at University of Manchester during the period from April 2014 to November 2017, except where otherwise stated. No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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Scientific contributions

Research findings from this thesis will all be published in peer-review journals. Chapter 3 and 5 are ready submission; chapter 4 is currently under reviewed by *Nature Communications*. Results generated from this thesis have contributed to 6 oral and 7 poster presentations as listed below:

**Oral presentations:**


Poster presentations:


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Chapter 1:

Introduction

1.1 Additive manufacturing

According to the American Society for Testing and Materials (ASTM) International, additive manufacturing (AM) is defined as "a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive methodologies". AM has many different synonyms, including Solid Freeform Fabrication (SFF), Rapid Prototyping (RP), Three-Dimensional Printing (3DP), Rapid Manufacturing (RM), Digital Manufacturing and E-manufacturing. AM covers over 30 different types of manufacturing technologies and has been widely used across different sectors, including automotive, aerospace, biomedical, energy storage, and jewellery, to name but a few.

AM offers many advantages over conventional manufacturing technologies. It has a high degree of design freedom, enabling parts to be produced with functionally graded materials, complex shapes and features, including freeform enclosed, hierarchical, cellular lattice, and auxetic structures, see an example in Figure 1. AM components are usually near-net shape; there is no need for assembly and additional tooling, e.g. welding and bolting, therefore manufacturers can build one-off products to shorten the product development cycle from days to hours.

Figure 1: Example of additive manufactured auxetic structures (after 23)
One of the key advantages of using AM technologies is the capability of producing parts with a buy-to-fly ratio of 1.5 - 2 : 1, whereas a machined part from as-cast or as-wrought material achieve a buy-to-fly ratio as 15 – 20 : 1. A buy-to-fly ratio is a ratio between the weight of a raw material and a finished part, i.e. the lower the buy-to-fly ratio, the higher the material conversion efficiency. A case study demonstrated that combining AM with topological optimisation can make a component with a better strength to weight ratio than that produced by conventional manufacturing technique (Figure 2). Moreover, powder bed fusion (PBF) AM technologies permits powder recycling up to 10 times without degrading the properties of the AM part. Therefore, AM is considered as a low carbon footprint manufacturing process owing to its low usage of materials and energy.

![Figure 2: Topological optimisation on additive manufactured bracket (after 28)](image)

Although AM offers a lot of opportunities, it also has a number of constraints in terms of materials, software, data management, sustainability, affordability, speed, reliability, intellectual property, and standards.

Currently, there are less than 50 alloy powders commercially available for AM, equivalent to 1 % of the alloy compositions (~ 5,500 alloys) for conventional manufacturing methods. Since many traditional alloys are susceptible to solidification cracking and hot tearing, combined with thermally induced stresses, these materials often lead to build failures during AM. Recently, Martin et al. introduced nano-particles into traditional crack-susceptible alloy powders and subsequently processed them by laser powder bed fusion (LPBF) to form AM parts with crack-free and grain refined microstructures. They emphasised that gaining a
fundamental understanding of AM processes is a key enabler in developing new materials and processes for AM.\textsuperscript{35,36}

Undoubtedly, advancement in novel computer simulation tools has enabled the predictions of laser-matter interaction\textsuperscript{37}, powder consolidation (\textit{e.g.} molten pool dynamics)\textsuperscript{38}, solidification (\textit{e.g.} microstructures), residual stresses\textsuperscript{39}, and mechanical properties of AM parts.\textsuperscript{40} However, some of the tools are computationally expensive, not very user-friendly and proprietary to an individual company or institution, limiting the rate of improvement in this field. Moreover, data validation is one of the key challenges to improve existing simulation models, resulting in a growing trend for collecting time-dependent data using \textit{in situ} monitoring devices inside AM machines.\textsuperscript{41} These monitoring devices can provide measurements of the surface temperature and the molten pool geometry over time. The future trend for AM technologies is to continue the advancement of a fully autonomous closed-loop system that can modify processing conditions during AM to optimise part quality.\textsuperscript{42,43}

The hardware of an AM machine also plays a major role in the pre-processing stage. A recent article reported that AM is facing data-management issues, \textit{e.g.} the PC of AM machines has insufficient memory to load a one-metre cube file.\textsuperscript{32} Therefore, upgrades and integration of new software and hardware in AM systems will continue to grow, however, this topic is beyond the scope of this project.

From an end-user perspective, Thomas \textit{et al.}\textsuperscript{44} and Kurfess \textit{et al.}\textsuperscript{45} pointed out that the costs of raw materials (16\%) and AM machines (66\%) were two major barriers to the adoption of AM technologies, see Figure 3. Notably, the cost breakdown structure of AM products is highly complex, which makes it difficult for a non-AM specialist to assess whether a part is more cost effective to be produced by AM or traditional manufacturing routes.

It is worth noting that the product cost is often linked with build accuracy and production rate of the AM process, and there are always trade-offs between these two factors. For example, the dimensional accuracy of a PBF AM is much better than wire arc additive manufacturing (WAAM) but a PBF system has a slower production rate than WAAM.\textsuperscript{9} PBF machines can only produce parts within the size of their powder bed, \textit{e.g.} a Concept laser cursing (M3) machine can build a part of slightly less than its build volume of 300 x 300 x 350
mm³, whereas WAAM machines can fabricate components, greater than a cubic metre in size as they are only limited by the moving range of the robotic arms. Hence, the end-users must consider these constraints at the onset of the product development cycle.

**Figure 3: Cost breakdown structure of a metal AM part (after⁴⁴)**

Given that almost every AM system is different from every other, machine qualification requires highly skilled operators to control and fine-tune build parameters before factory acceptance. However, most commercial machines are built with a closed architecture and prohibit operators from making detailed changes, slowing down the qualification process and the adoption of AM technologies.

Scan-To-Print technologies are becoming increasingly popular as the AM market expands. Users can capture a 3D object within minutes into digital formats using mobile devices, and subsequently, convert these digital files to print. This enables end-users to create and modify computer-aided design (CAD) drawing files for the next generation of products. They also allow the end-users to make counterfeit goods or products, resulting in copyright infringement issues.⁴⁵

In summary, AM technologies are considered as disruptive and revolutionary, showing great promise to produce products with unique capabilities. However, there are many other facets of the eco-system that need addressing in order to speed up the adoption of AM technologies.
1.2 Aim

This thesis focuses on the material science aspect of the eco-systems, in particular, studies of the laser-matter interaction and powder consolidation during LAM, because they have been proven difficult to characterise and hence are not well understood. The aim of the thesis is to capture the missing physics behind these phenomena using in situ, non-destructive and real-time experimental techniques, providing real-time data to verify and validate existing simulation models. Hopefully, the experimental techniques and results reported from this thesis will stimulate the development of other experimental and simulation techniques to predict, control and optimise the AM process.

1.3 Objectives

The aim of the thesis is divided into following objectives:

1) To design, develop and commission an experimental apparatus that permits real-time and in operando studies of laser-matter interaction and powder consolidation during laser additive manufacturing (LAM) using high-speed synchrotron X-ray radiography.

2) To observe and elucidate the evolution of molten pool, melt track and defects (such as porosity and spatter) as well as the melt flow behaviour with and without the presence of oxide during LAM.

3) To develop image processing algorithms for the quantification of molten pool geometry (e.g. width, depth, and area) over time and solidification shrinkage (%) of the melt track as it cools.

4) To correlate these results with respect to the laser power ($P$), scan speed ($v$) and linear energy density ($LED$).

The structure of the thesis will be presented as follows:

Chapter 2 reviews the state of the art research on laser-matter interaction, powder consolidation, and solidification in LAM and highlights the current research gaps in the field.

Chapter 3 details the design, development, and applications of the laser additive manufacturing process replicator (LAMPR). It shows an example of combining LAMPR with
synchrotron X-ray imaging to study LAM of stainless steel (SS316L) and bioactive glass (13-93).

Chapter 4 focuses on laser-matter interaction and powder consolidation of Fe-Ni alloy (Invar 36) during LAM. It reveals many mechanisms involved in the evolution of melt tracks, porosity and spatter, also uncovers new mechanisms of pore migration, dissolution, and dispersion.

Chapter 5 emphasises on defect formation mechanisms during LAM and provided detailed explanations on the formation of porosity (e.g. open pore) and droplet spatter. It also highlights the effects of oxide on the fluid flow inside the melt track and porosity formation.

Chapter 6 summaries key findings from the results chapters 3 - 5. The laser beam characterisation and detailed information of the laser system are included in Appendix I. Chapter 7 describes the future work beyond the scope of the PhD.
Chapter 2:

Literature review

2.1 Laser additive manufacturing

Laser additive manufacturing (LAM) uses a laser beam to consolidate powder into a high dense object. It splits into two categories: Laser powder bed fusion (LPBF) and laser metal deposition (LMD,) or also termed as direct energy deposition (DED).1,46

2.1.1 Laser powder bed fusion (LPBF) additive manufacturing

LBPF is also known as selective laser sintering (SLS)47, selective laser melting (SLM)48 and direct metal laser sintering (DMLS)46. Its basic principle is illustrated in Figure 4.

![Figure 4: The basic principles of laser powder bed fusion (LPBF) technology](image)

Users produce a CAD drawing of the AM parts, and subsequently convert them into a Standard Tessellation Language (.stl) file format using a 3D CAD software package, e.g. AutoCAD. The .stl file represents a 3D model as a set of triangles, where each triangle is defined by its normal vectors and vertices.6 Once, the users transfer the .stl file to a LBPF machine, they can define the size, position, and orientation of the 3D model. After they confirm the machine parameters, the 3D model is divided into a series of 2D slices with a predetermined thickness along the build direction of the part. At the onset of LPBF process, a thin powder layer deposits onto a build platform. Then, a focused laser beam with a peak
power density of $> 10^6 \text{W cm}^2$ selectively fuses the powder particles together according to the build features on each 2D slice. Next, the build platform lowers down, followed by another powder layering and powder fusion, these steps repeat on a layer-by-layer basis until the 3D part is built (Figure 4). In the final stage, users extract the AM part from the LPBF machine and they use a vacuum cleaner or brush to remove the excess powder on the part surface. Similar to traditional manufacturing, AM parts may be subjected to other post-processing stages to improve their properties or aesthetic appearance, including heat-treatment, hot isostatic pressing (HIP) and laser polishing.

2.1.2 Laser metal deposition (or direct energy deposition)

In LMD (or DED), a focused laser beam melts either a powder or wire feedstock as it is being deposited onto a workpiece. A typical powder based LMD system (Figure 5) consists of a platform and a laser deposition head coupled with a coaxial powder delivery system. The LMD can operate with a stationary platform while moving the deposition head, or vice versa. In advanced LMD systems, additional sensors and real-time monitoring devices are installed to control the laser power, scan speed, powder feed rate and molten pool geometry during the AM build. Inside the deposition head, a fibre laser is coupled with a series of focusing optics for changing the spot size and shape of the laser beam. The powder nozzle(s) is attached at the bottom of the deposition head and connected to a powder delivery system. The powder feedstock flows via the powder delivery system towards the centre of the nozzle by a carrier gas, e.g. argon. Concurrently, the high energy laser beam melts the powder at a proximity to the substrate to form a melt droplet, which then deposits onto the workpiece. Melting and deposition of powder repeat on a layer-by-layer basis until the AM part is built. LMD is a versatile AM technology that can coat, build and repair components. However, the design freedom of LMD is much more limited compared to that of LPBF, and it is difficult to produce small intricate features by LMD, e.g. lattice structures and internal channels.
Figure 5: A schematic diagram of a powder based LMD system (after 6)

2.2 Technological challenges in LAM

LAM offers great promise across many different industries; however, the uptake of such technologies is hindered by several technical challenges linking to the build quality of the AM component, in terms of part properties and dimensional accuracy. AM parts are often reported to exhibit inconsistent part properties, e.g. mechanical\textsuperscript{22,51–53}, thermal and electrical properties\textsuperscript{15}. These variations in properties have been related to the anisotropy of microstructural features of the AM part\textsuperscript{52,53}, including: (1) grain morphology; (2) crystallographic texture; (3) processing defects, e.g. porosity\textsuperscript{54}, oxide films\textsuperscript{55} and spatter\textsuperscript{51}, (4) poor surface finish\textsuperscript{56,57} and (5) undesired residual stresses\textsuperscript{39,48}. The last three factors are known to be detrimental to mechanical properties of the AM parts\textsuperscript{11,58}. The dimension of the as-built AM part often deviates from the CAD drawing owing to the part distortion induced by solidification shrinkage and accumulation of residual stresses\textsuperscript{7}. Figure 6 illustrates this build accuracy issue between the as-built AM part and the CAD drawing. There are other technical problems associated with build angles\textsuperscript{59} and overhang structure\textsuperscript{41} as shown in Figure 7. Note that the overhang structure describes a feature that builds on top of loose powder.
Figure 6: 3D rendering of a LPBF benchmark sample structure: a, The CAD design; b, micro-computed tomography (micro-CT) volume and c, a rendered image after applied image registration on (b) with reference (a).59

The resultant thermal, microstructural and mechanical properties of the AM part are governed by the solidification and process parameters, including laser characteristics, process environment and material properties. The physical understanding between the onset of the laser-matter interaction and solidification is still insufficiently understood owing to the complex molten pool behaviour that occurs in very short time intervals. Many existing process simulation models have made assumptions to fill the knowledge gap, therefore they may not provide accurate predictions. To resolve the aforementioned challenges, there is a need to acquire a better understanding of the laser-matter interaction, powder consolidation and solidification in LAM, including melt pool dynamics, e.g. flow characteristics. This will lead to a greater ability to predict and control the microstructure of the AM part, ultimately fabricating parts with better performance and consistent quality.

Figure 7: 3D rendering of a LPBF benchmark which consists of 7 different fins. Each fin was built at a different elevated angle ranging from 0° - 90°. Box A highlights distortion as a result of accumulation of residual stresses and box B highlights poor surface finish due to overhang structure59
2.3 Physical phenomena in LAM

The build quality of AM components is linked to their manufacturing process and microstructures; therefore, the understanding of such relationships is essential for optimising the build quality. Over the past three decades, extensive studies have been carried out to develop theories for explaining the process-microstructure-property relationship albeit many of them are still incomplete.\textsuperscript{35,60} This section reviews the state of the art studies on this topic and addresses the future research directions.

2.3.1 Background

The LAM process can be divided into three stages, including: 1) the laser-matter interaction, 2) powder consolidation, and 3) solidification (Figure 8). During the laser-matter interaction, some of the incoming laser beam is absorbed, transmitted or reflected (or scattered) by the powder (Figure 8a). Once the powder absorbs sufficient laser energy, it undergoes melting and forms a molten pool (Figure 8b). Meanwhile, the molten pool dissipates some of its heat energy to sinter the surrounding particles. The sintered powder layer is usually found along the edges or at the bottom of a build feature, increasing the surface roughness of the AM part (Figure 8b). When the input laser energy is high, the laser beam vaporises the low boiling point elements from the molten pool. A further increase in input laser energy, the laser beam ionises the metal vapour and forms a plasma. A further discussion on this topic can be found in section 2.4.

In Figure 8c, the temperature at the centre of the molten pool ($T_b$) is much higher than that on both sides of the molten pool ($T_a$ and $T_c$), which develops a temperature gradient across the molten pool surface. This promotes a fluid inside the molten pool to flow from a region with a high surface tension (the edges) to the bottom of the molten pool, and then from the bottom of the molten pool to a region with a low surface tension (the centre), and recirculate again, see details in section 2.4.3. This phenomenon is known as Marangoni convection. As the molten pool cools down rapidly, it transforms into a crystalline or amorphous solid via solidification or vitrification. Lastly, the solid undergoes a volume contraction as it cools.
Figure 8: Underlying physical phenomena behind LAM on loose powder: a, Laser-matter interaction, where 1, 2 and 3 indicate laser absorption, reflection and scattering, respectively. b, Powder consolidates into a molten pool and a sintered powder layer. c, Solidification of a molten pool, where the blue arrows indicate the direction of the crystal growth.

2.3.2 Laser-matter interaction

The laser-matter interaction depicts a process when a laser beam at a given wavelength ($\lambda$) interacts with the powder particles. The efficiency of the laser-matter interaction ($\eta$) depends on the laser beam properties (such as the $\lambda$, laser power, and spot size), optical properties of the powder (such as absorptivity ($A$), reflectivity, and refractive index as a function of temperature) and the particle size distribution (PSD). The laser absorption mechanisms involve collisions between electrons-electrons, electrons-photons, and electrons-defects. The first two terms are related to the intrinsic properties of the powder. In the last term, the defects are referred to surface cracks, oxide films or impurities (e.g. transition metal oxides (TMOs) in the powder particles, all of which could enhance their laser absorption.

Fischer et al. summarised laser absorption mechanisms into absorptions at the powder surface and inside the powder bed, i.e. powder-coupling and bulk-coupling, respectively. They highlighted that the optical penetration depth of the powder material (~100 $\mu$m) is a few orders of magnitude greater than the bulk material (~0.1 $\mu$m) due to the multiple reflections from the powder surfaces. The higher the optical penetration depth, the more laser energy is likely to be absorbed by the powder.
The effective absorptivity ($A^*$) of the powder bed can be measured by a micro-calorimetry method\textsuperscript{65,66} and predicted by ray-tracing methods\textsuperscript{37,61,65}. Notably, the $A$ of the powder is key to determine $\eta$, and thus they can be used to calculate the amount of energy that has contributed to the powder consolidation and solidification processes.

In general, the $A$ of metals increases with temperature and decreases with $\lambda$ (Figure 9). Therefore, processing of metal powders by a Nd: or a Yb: based laser ($\lambda = 1.03 – 1.07 \mu m$)\textsuperscript{55,67–70} requires much less laser power to produce high density AM parts than those produced by a CO$_2$ laser ($\lambda = 10.6 \mu m$)\textsuperscript{71,72}. In particular, AM of highly reflective materials, e.g. Au, Cu and their alloys, using a laser at $\lambda$ of $\sim 1 \mu m$ remains challenging due to their weak absorption at this $\lambda$.\textsuperscript{73,74}

![Absorptivity (A) of pure metals at various laser wavelengths (\lambda) (after\textsuperscript{75})](image)

**Figure 9:** Absorptivity ($A$) of pure metals at various laser wavelengths ($\lambda$) (after\textsuperscript{75})

Boley \textit{et al.}\textsuperscript{37} proposed to use a bimodal PSD to achieve an optimum number of multiple reflections in the powder bed that improves the laser absorption of highly reflective materials. Recently, Heussen \textit{et al.}\textsuperscript{76} demonstrated an alternative method to process highly reflective materials using a green laser ($\lambda = 515$ nm). Others have suggested that highly reflective materials can be processed by a high-intensity laser beam\textsuperscript{70}, with a long exposure time or a slow scanning speed.\textsuperscript{75}
2.3.3 Powder consolidation

Kruth et al.\textsuperscript{35} and Gu et al.\textsuperscript{46} highlighted four possible powder consolidation mechanisms in AM, see a summary flow chart in Figure 10. Powder consolidation involves fusion of powder particle into a dense object including solid-state sintering (SSS), laser sintering (i.e. liquid phase sintering (LPS) or partial melting), and laser melting (i.e. full melting and chemical-induced binding).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{powder-consolidation-diagram.png}
\caption{Overview of different powder consolidation mechanisms in LAM}
\end{figure}

2.3.3.1 Solid state sintering (SSS)

Solid state sintering (SSS) describes sintering of particles into a coherent solid structure at an elevated temperature that is below the solidus temperature of the powder.\textsuperscript{77} SSS is mainly driven by a combination of particle rearrangement and rotations, local deformation, grain growth, and a range of diffusion mechanisms (Figure 11).\textsuperscript{78} In LAM, the laser-matter interaction, powder consolidation, and solidification take place in the range of $10^{-3}$ to $10^{-6}$s\textsuperscript{35,46} whereas a typical SSS process takes hours or longer to complete\textsuperscript{79}, hence SSS rarely occurs under normal LAM conditions. Perhaps, SSS may take place if a prolonged preheating stage is being used during AM. For example: In anchorless SLM, Vora et al.\textsuperscript{80,81} raised the preheat temperature of the powder bed just below the eutectic temperature of the powder material.\textsuperscript{80,81} If a large AM part is built using anchorless SLM, the powder bed is subjected to a high preheat temperature over a long period, increasing the likelihood for SSS to occur. However, there are no reports on the side effects of anchorless SLM.
**Figure 11**: Illustration of SSS using a three-sphere model. The numbers represent different diffusion mechanisms: (1) from surface by surface diffusion; (2) from surface by bulk diffusion; (3) from surface by evaporation/condensation; (4) from grain boundary by boundary diffusion; (5) from grain boundary by bulk diffusion; (6) from bulk by bulk diffusion through dislocations (after 79)

### 2.3.3.2 Laser sintering

Laser sintering occurs when the laser energy is only sufficient to melt the skins of the powder particles to produce a small amount of liquid to form a coherent solid network. There are two types of laser sintering: liquid phase sintering (LPS) and partial melting.82

LPS is an indirect laser sintering method that sinters a mixture of binder and structural powder materials together by heating the powder mixture near the melting temperature of the binder material.83 The binder material has a lower melting point and a smaller particle size than the structural materials.83

Partial melting is a direct laser sintering method which does not require a binder.84 Unlike LPS83 (Figure 12), partial melting does not involve solution precipitation nor SSS, it binds the powder together to form a green part with a high degree of porosity. This has been widely reported across a range of materials, including Al-5,71,85, Cu-86, Fe-87 and Ti-88 based powders.
Therefore, the additive manufactured green parts often required additional post-processing steps to achieve full density, including hot isostatic processing (HIP)\textsuperscript{90,91} or liquid infiltration\textsuperscript{82,85,89,92}. However, Sercombe and Shaffer\textsuperscript{85} reported that the microstructure produced by SLS with liquid infiltration could lead to poor structural integrity or formation of a crack susceptible skeleton network (Figure 13). Both effects are detrimental to the mechanical performance of the AM part.

Figure 12: A schematic diagram of two different LPS mechanisms (after \textsuperscript{89})

Figure 13: Microstructure of the 6061–2%Mg–1%Sn–4%nylon green part a, before metal infiltration and b, after infiltration with Al–14.3%Si–4.7%Mg. The light grey indicates the Al grains. The dark grey indicates the nitride film. The black indicates the binder material in (a) and voids/cracks in (b). (after \textsuperscript{5})
2.3.3.3 Laser melting

Laser melting consolidates powder materials into fully dense AM parts via full melting and chemically induced binding. Full melting occurs when there is sufficient laser energy to completely fuse the powder particles together to form a molten pool. Then, the molten pool binds with the previous scanned feature to form a track and by combining multiple tracks together to form a part.48

During the laser-matter interaction, it is also possible to form a compound via an in situ chemical reaction between two powders, i.e. chemically induced binding. Lu et al.93, Dadbakhsh et al.94 and Gu et al.95 utilised chemically induced binding to form thermodynamically stable metal matrix composites (MMCs) by LAM. These MMCs retain excellent mechanical properties, wear and corrosion resistance at elevated temperature. Notably, Gu et al.95 have extensively investigated a number of in situ MMCs by LAM, including TiC in alloy matrices of Inconel 71896, AlSi10Mg97, Ti–Al98 and Ti5Si399. They also explored many other types of MMCs, such as TiN/Ti5Si3100, WC/Ni101 and Al5Si4O10/Al102. From these studies, they found that the prediction and control of these microstructures produced from chemically induced binding was very challenging. Gu et al.98 also reported that the TiC grain morphology altered from layered to octahedral, truncated octahedral and near-spherical with increasing laser power. Defects (e.g. gas entrapment, particulate aggregation and interfacial micro-cracks) and poor wettability of the liquid matrix on ceramic phase are the main obstacles to obtain fully dense MMCs by LAM.95

2.3.3.4 Solidification in LAM

The microstructure development in metal AM is mainly controlled by the process parameters given in Equation 1.103 The cooling rate (ε) is the product of the thermal gradient (G) and solidification rate at the solid-liquid interface (R). G depends on the temperature of liquid and the freezing temperature of the material whereas R depends on the laser scan speed (v) and the angle (α) between the directions of the moving laser beam and crystal growth, as shown in Equation 2.67
\[ \varepsilon = GR \]  \hspace{1cm} \text{Equation 1}

\[ R = v \cos \alpha \]  \hspace{1cm} \text{Equation 2}

Heterogeneous nucleation \( \Delta G_{\text{het}} \) can be expressed as a product of homogenous nucleation, \( \Delta G_{\text{hom}} \), in \textbf{Equation 3} and the shape factor, \( S(\theta) \), \textbf{Equation 4}. The wetting angle \( \theta \) between the substrate (loose powder or a solid) and molten pool is between \( 0^\circ \leq \theta \leq 180^\circ \), such that \( 0 \leq S(\theta) \leq 1 \), and hence \( \Delta G_{\text{het}} \leq \Delta G_{\text{hom}} \). Heterogeneous nucleation is more energetically favourable than homogenous nucleation in LAM.

\[ \Delta G_{\text{het}} = \Delta G_{\text{hom}} (S(\theta)) \]  \hspace{1cm} \text{Equation 3}

where:

\[ S(\theta) = (2 + \cos \theta) \frac{(1-\cos \theta)^2}{4} \]  \hspace{1cm} \text{Equation 4}

The \( \varepsilon \) controls the grain size, \textit{e.g.} the higher \( \varepsilon \), the finer the grain size and vice versa. The \( (G/R) \) ratio controls the grain morphology, \textit{e.g.} decrease in \( (G/R) \) ratio, the grain morphology changes from cellular to columnar dendritic to equiaxed dendritic.\textsuperscript{104} \( G \) and \( R \) values are constantly changing as the molten pool cools, they are controlled by the heat input as a function of laser parameters.

There are other alternative methods to control the grain structure and morphology without changing the heat input, including the addition of grain refiners, laser scanning, and seeding strategies. Martin \textit{et al.}\textsuperscript{34} utilized additions of inoculants to achieve grain refined microstructures of Al-based alloys and mitigate solidification cracking during AM. Morgan \textit{et al.}\textsuperscript{105} highlighted that different scan strategies could alter grain structure and morphology; Thijs \textit{et al.}\textsuperscript{67} found that island scan strategy could produce parts with the lowest texture index, \textit{i.e.} a microstructure with the least anisotropy. Basak and Das\textsuperscript{106} introduced scanning laser epitaxy (SLE) to nucleate grains that follow the grain morphology from the underlying substrate.
2.4 Key factors influencing the physical phenomena of LAM

There are many other factors influencing the physical phenomena in LAM, including process parameters (2.4.1), process environment (e.g. gas type, flow rate, etc.)\textsuperscript{42}, powder and bulk properties (2.4.4).\textsuperscript{107} The following sub-sections provide some general understanding about the relationship between these factors and the physical phenomena of LAM.

2.4.1 Process parameters

As discussed in section 2.3.3.4, the heat input is governed by the process parameters (Table 1) which influence the development of microstructures in LAM.

Table 1: Key process parameters in LAM

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>Symbols</th>
<th>Units</th>
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<tbody>
<tr>
<td>Laser power</td>
<td>$P$</td>
<td>W</td>
</tr>
<tr>
<td>Spot size</td>
<td>$d$ or $2r$</td>
<td>mm</td>
</tr>
<tr>
<td>Scan speed</td>
<td>$v$</td>
<td>mm/s</td>
</tr>
<tr>
<td>Hatch spacing</td>
<td>$h$</td>
<td>mm</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>$t_{\text{thickness}}$</td>
<td>mm</td>
</tr>
<tr>
<td>Exposure time</td>
<td>$t_{\text{exp}}$</td>
<td>µs</td>
</tr>
<tr>
<td>Point distance</td>
<td>$d_{\text{point}}$</td>
<td>µm</td>
</tr>
</tbody>
</table>

From Equation 5, the first term explains that the absorbed laser power density is a product of the coupling efficiency ($\eta$) of a given material and the laser power density which is calculated by dividing the input laser power ($P$) by the area of the laser spot size ($\pi r^2$). Using the absorbed laser power density and laser-matter interaction time, it is possible to predict whether a material undergoes heating, melting or vaporisation.\textsuperscript{108}

\[
\text{Absorbed laser power density (W/mm}^2) = \eta \frac{P}{\pi r^2}
\]  

Equation 5

However, the interaction time is missing in Equation 5 which can be determined by the type of laser system is being used in the LAM machine, \textit{e.g.} a continuous wave (CW) laser with or without modulation. For a CW laser without modulation, the main process variable
associated with time is $v$, and thus the energy density ($ED$) can be expressed as shown in Equation 6.\textsuperscript{109}

$$\text{Energy density, } ED \left( \frac{J}{mm^2} \right) = \frac{P}{\pi r^2} \frac{2r}{v} \frac{2r}{h}$$

Equation 6

The $ED$ describes how much energy is being delivered onto the powder material per unit area which can be simplified as the Andrew number ($A_N$) in Equation 7.\textsuperscript{110}

$$\text{Andrew number, } A_N \left( \frac{J}{mm^2} \right) = \frac{P}{v h} \approx ED$$

Equation 7

In many early AM studies, the powder consolidation process is mainly examined by producing multiple single line scans with different $ED$ at constant $h$ and $t_{\text{thickness}}$.\textsuperscript{111–113} This is also known as the linear laser energy density ($LED$) as given in Equation 8.

$$LED \left( \frac{J}{mm} \right) = \frac{P}{v}$$

Equation 8

Simchi et al.\textsuperscript{114} added a variable $t_{\text{thickness}}$ in Equation 7 to calculate the total energy input per unit volume of materials or the volume energy density ($VED$), see Equation 9\textsuperscript{114}:

$$Volume \text{ energy density } \left( \frac{J}{mm^3} \right) = \frac{P}{v h t_{\text{thickness}}}$$

Equation 9

Equation 10\textsuperscript{115} is another form of Equation 9 for a CW laser with a modulation configuration, where $\frac{1}{v}$ from Equation 9 is replaced by the term $\frac{t_{\text{exposure}}}{d_{\text{point}}}$.

$$Resulting \text{ energy input, } Q \left( \frac{J}{mm^3} \right) = \frac{P}{h t_{\text{thickness}}} \frac{t_{\text{exposure}}}{d_{\text{point}}}$$

Equation 10

Undoubtedly, the $VED$ or $Q$ is one of the most widely adopted variables to benchmark or qualify LAM machines and products, because it shows a strong positive correlation with many production outcomes, including part density\textsuperscript{114}, the volume fraction of phases, secondary dendrite arm spacing\textsuperscript{116}, surface roughness\textsuperscript{115} and mechanical properties\textsuperscript{115}. 42
Over a range of studies, the typical outcomes with various VED can be summarised as follows.\textsuperscript{11,35,58} According to Equation 5, a high VED can be achieved by using a combination of high $P$ as well as low $v$, $t$, and $h$. A laser beam with a high VED forms a molten pool with a high surface temperature which improves its wettabiliy by reducing its viscosity and surface tension).\textsuperscript{117} Good wettabiliy enables the molten pool to spread onto the previous layer or fuse with the neighbouring tracks. In general, a high VED increases part density and enhances the mechanical performance of the AM part.\textsuperscript{70}

When the VED is too high, the laser beam vaporises the low boiling point elements (e.g. Zn and Mg, etc.)\textsuperscript{67,70,118} in the molten pool and generates a metallic plume (or plasma)\textsuperscript{108} which reduces the laser-matter coupling efficiency due to a combination of absorption and scattering by the plume.\textsuperscript{119} He et al.\textsuperscript{120} described that some of the laser energy can be absorbed during the plasma-electron ion collisions, also known as the Inverse Bremsstrahlung absorption. In addition to absorption, the nanoparticles constituted in the plasma cause scattering of the laser beam and attenuating the laser power by: (1) Rayleigh scattering and (2) Mie scattering. Rayleigh scattering applies when laser beam scatters by small, dielectric and spherical particles having a diameter ($d$) considerably smaller than the wavelength of the laser beam\textsuperscript{108}, i.e. Rayleigh scattering occurs when $d < \frac{\lambda}{10}$. Mie Scattering occurs when the particle size is comparable to the wavelength ($\lambda$) of the laser beam\textsuperscript{121}, i.e. Mie scattering occurs when $\frac{\lambda}{10} < d < \lambda$.

During the laser-matter interaction, the metallic plume exerts a recoil pressure near the laser-matter interaction zone which flattens the molten pool, resulting in a smooth track surface. In particular, a combination of high $P$ and low $v$ induces a molten pool instability which leads to powder entrapment (e.g. lack of fusion defect), gas entrapment (e.g. gas porosities)\textsuperscript{118,122,123}, formation of large irregular pores (e.g. keyhole porosities\textsuperscript{67,124}) and grain coarsening (e.g. increased the secondary arm spacing)\textsuperscript{67,116,118}, see schematic diagram in Figure 14. However, some of the underlying defect formation mechanisms are not well understood because it is difficult to probe inside the melt tracks during LAM.

In contrast, a low VED can be achieved by reducing $P$ while increasing $h$, $t$ and $v$. A combination of low $P$ and high $t$ causes insufficient laser melting, this leads to the formation of
large irregular pores\textsuperscript{48,113}, resulting in a low part density and poor mechanical performance. Increasing $v$ increases $\varepsilon$ (Equation 1) which produces a fine grain structure (Equation 2), enhancing the mechanical properties. Notably, there is a limitation on how fast the laser beam can move.

\begin{align*}
\frac{\pi d}{L} > \sqrt{\frac{2}{3}} \quad \text{(Equation 1)}
\end{align*}

\begin{align*}
\frac{d}{L} > \sqrt{\frac{2}{3}} \quad \text{(Equation 2)}
\end{align*}

\textbf{Figure 14}: Schematic of different types of defects found in LAM: (a) keyhole porosity (after\textsuperscript{124}), (b) open pores, (c) residual gas porosity, (d) gas porosity, (e) powder entrapment, and (f) lack of fusion (after\textsuperscript{125}).

At a very high $v$, the surface temperature of the molten pool significantly reduces while raising the surface tension and viscosity of the molten pool. This causes a melt track to break up into individual droplets and promote spheroidisation\textsuperscript{35}, \textit{i.e.} balling (\textbf{Figure 15}). Balling increases the porosity and surface roughness of the AM part\textsuperscript{55}, it may inflict damage to the recoater blade during powder deposition\textsuperscript{126}. The balling phenomena had been widely investigated in AM of different powder materials, including Au\textsuperscript{74}, W\textsuperscript{127}, Al-based\textsuperscript{55}, Cu-based\textsuperscript{73}, Fe-based\textsuperscript{48,126,128} and Ti-based alloys\textsuperscript{129}.

Several studies proposed that balling was induced by a form of Plateau-Rayleigh instability.\textsuperscript{35,113,130} Yadroistev \textit{et al.}\textsuperscript{113} proposed that balling occurred when the molten pool diameter ($d$) to length ($L$) ratio satisfied this condition: $\frac{\pi d}{L} > \sqrt{\frac{2}{3}}$. Zhou \textit{et al.}\textsuperscript{127} hypothesised
that balling occurred when the solidification time of molten pool was faster than the spreading
time of the molten pool, such that balling minimises the surface energy for solidification. Note
that the solidification and spreading times are related to the intrinsic powder properties, e.g.
viscosity and surface tension, etc. Other studies have shown that a high oxygen level of > 0.1
% combined with low P favours the formation of balling.\textsuperscript{126,127} These theories are mainly based
on \textit{ex situ} characterisations; to the best of the author’s knowledge, there are no \textit{in situ}
observations that capture the morphological transformation of a hemi-cylindrical track into
spherical or ellipsoidal molten beads. Therefore, future work is needed to validate these
theories.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure15.png}
\caption{SEM images showing a morphological transition of single scan tracks that changes
from hemi-cylindrical tracks to a series of spherical beads with increasing v (after \textsuperscript{126})}
\end{figure}

Some studies argued that \textit{VED} was not the best indicator to describe the powder
consolidation phenomena in LAM. Gu \textit{et al.}\textsuperscript{131} reported that AM parts produced by a constant
\textit{VED} (with different combinations of \textit{P} and \textit{v}) exhibited a large variability in porosity from 0.4
to 5.4 \%. Prashanth \textit{et al.}\textsuperscript{132} reported similar findings and highlighted that \textit{P} was the most
influential process parameter in \textbf{Equation 9}, such that a reduction in \textit{P} deteriorated the
mechanical properties and density of the AM part.

Instead of using \textit{VED}, Kruth \textit{et al.}\textsuperscript{48} used a \textit{P-v} process window to study the powder
consolidation phenomena in LAM (\textbf{Figure 16a}). The \textit{P-v} process window has been widely
adopted by the AM community to study the build quality of AM parts with respect to the powder
characteristics and process parameters. Similarly, Beuth \textit{et al.}\textsuperscript{133}, Gockel \textit{et al.}\textsuperscript{133} and Clymer
et al.\textsuperscript{134} developed a \(P\)-\(v\) process design chart that combined the results from the \(P\)-\(v\) experiments and model simulations to predict the solidification modes, molten pool geometry, part density, mechanical strength, surface finish, and build precision in a DED process, (Figure 16b). This design chart is also applicable to other AM processes.

![Figure 16: a, Process window of Fe-based alloy (after\textsuperscript{148}) by SLM and b, a \(P\)-\(v\) design chart for the prediction of solidification modes in DED (after\textsuperscript{135}).](image)

### 2.4.2 Effects of viscosity and surface tension

Undoubtedly, the intrinsic properties of the powder materials affect the laser-matter interaction (2.3.2), powder consolidation (2.3.3) and solidification (2.3.3.4) in LAM. In particular, the viscosity and surface tension of the molten pool have a strong influence on the final shape, geometry, microstructure, and properties of the melt track. This relationship can be described by the Marangoni number \((Ma)\textsuperscript{136}\) which correlates the dynamic viscosity and surface tension of the molten pool as a function of temperature. \(Ma\) is a measure of the strength of the convective heat transfer in the molten pool during AM as given in Equation 11:

\[
Ma = \frac{\rho \Delta T}{\mu \alpha \Delta T}
\]

\textbf{Equation 11}

Where \(\frac{\Delta T}{\Delta T}\) is the temperature coefficient of surface tension, \(w\) is the width of the molten pool, \(\Delta T\) is the temperature difference between the maximum temperature of the molten pool and solidus temperature of the material, \(\alpha\) is the thermal diffusivity and \(\mu\) is the dynamic viscosity which can be calculated according to Equation 12:\textsuperscript{95}:
Dynamic viscosity, $\mu = \frac{16m}{15\sqrt{kT}\gamma}$ \hfill Equation 12

where $m$ is the atomic mass, $k$ is the Boltzmann constant, $T$ and $\gamma$ are the temperature and the surface tension of the molten pool, respectively.

For most metallic systems (in the absence of surfactants), $\frac{dy}{dT} < 0$, therefore $\mu$ decreases with increasing $T$.\textsuperscript{137} Under normal AM process conditions, most metals are expected to follow an outward centrifugal Marangoni convection (Figure 17a). With the presence of surfactants in the molten pool, e.g. sulphur and oxides in steel alter the $\frac{dy}{dT} < 0$ to $\frac{dy}{dT} > 0$,\textsuperscript{138} they change the flow pattern from an outward to an inward Marangoni convection, i.e. centripetal convection (Figure 17b). The centripetal convection is a temporary effect, Lee et al.\textsuperscript{139} predicted that the coefficient of surface tension of the molten pool produced by Gas Tungsten Arc welding would eventually alter from a positive to negative value. Kidess et al.\textsuperscript{140} explained that all the surfactant molecules dissociated at a critical temperature, and hence the liquid will start to behave as the pure liquid metal.

Figure 17: Schematic of Marangoni convection: a, an outward centrifugal Marangoni convection when $\frac{dy}{dT} < 0$ and b, an inward centripetal convection when $\frac{dy}{dT} > 0$ (after 141)

The negative sign in Equation 11 cancels out the negative sign of $\frac{dy}{dT}$. The higher the Ma the higher the heat input to the molten pool, this induces a high convective heat transfer, resulting in a fast fluid flow inside the molten pool. Khairallah et al.\textsuperscript{38} predicted that the flow velocity of the fluid could be as high as 4 m/s. As a consequence, this increases the depth to width ratio of the molten pool.\textsuperscript{142,143} A high Ma can reduce lack of fusion defects\textsuperscript{136} and oxide-
led defects. However, when $Ma$ becomes too high, it causes molten pool instabilities and leads to the formation of keyhole pores. As a high intensity laser beam interacts with the powder bed, it causes the powder particles and part of the metal substrate to vaporise. As a result of that, a vapour cavity forms in the substrate which increases the laser absorption and penetration depth. When the laser-matter interaction completes, the molten pool undergoes rapid solidification and there is insufficient liquid to fill the cavity, resulting in irregular pores, also known as the keyhole pores. Khairallah et al. also predicted that Marangoni convection cooled down the molten pool and promotes the formation of a powder-free (denudation) zone via spattering, i.e. ejection of powder or molten materials near the laser-matter interaction zone.

### 2.4.3 Effects of oxide

The presence of oxide films alters the $\frac{dy}{dT}$ from negative to positive, which also changes the heat, mass and momentum transfer in the molten pool dynamics. This sub-section highlights the effects of oxide on the LAM process (e.g. molten pool dynamics) and the resultant part properties. It also summarises possible methods to minimise the effects of oxide.

Al is an example material that has a high affinity for oxygen, its surface is usually covered with a thin oxide film up to 15 nm thick. Ravi et al. reported that the oxide film drastically raised the surface tension of the molten Al by ca. three times than that without the presence of oxide. Li et al. suggested that the oxide reduced the wettability of the liquid metal on a substrate which led to the balling phenomenon. Olakanmi et al. hypothesised that the oxide films restricted heat transfer from one particle to another and hence reduced the effective thermal conductivity of the powder bed. Sames et al. linked that the low thermal conductivity powder bed would promote balling or swelling on subsequent layers due to the localised hot spot. Swelling describes the rise of solid material above the plane of powder bed.

Olakanmi et al. suggested that the addition of Mg could reduce the surface tension of molten Al, in addition, Schaffer et al. postulated that the Mg would react with $\text{Al}_2\text{O}_3$ to form a spinel phase of $\text{MgAl}_2\text{O}_4$ (Equation 13) and this chemical reaction may disrupt the $\text{Al}_2\text{O}_3$ during LAM and improve the part density.
Olakanmi et al.\textsuperscript{107} found that the laser-induced circumferential stress was insufficient to overcome the fracture stress of spinel, therefore the spinel phase would still remain in the microstructure. Tang et al.\textsuperscript{149} examined these oxide films and hypothesised that the formation of the spinel phase originated from the metal vaporisation during LAM. The aforementioned studies emphasised that the challenges of processing materials with a high affinity for oxygen. Undoubtedly, the reduction of oxygen pickup on the powder particles and disruption of oxide films during LAM are crucial for achieving high-density parts.

Sutcliffe et al.\textsuperscript{150} suggested that it may be possible to prevent oxide formation during SLM by lowering the oxygen concentration < 10\textsuperscript{-52} bar inside the build chamber. However, this requires an ultra-high vacuum build chamber which is costly and not attractive for industrial application. They also proposed to use an Al alloy composition with a small addition of Bi to reduce oxide formation via chemically induced binding of Bi and the oxide.\textsuperscript{150} Alternatively, Louvis et al.\textsuperscript{55} used a high laser power (> 150 W) and a low oxygen environment (0.1 - 0.2 %) to vaporise some of the surface oxide films in Al alloy. Buchbinder et al.\textsuperscript{70} further increased the laser power to 1 kW to process Al and reported that the oxide layer was completely disrupted or vaporised to produce 99.9% dense Al parts. In 2012, the production cost of a fibre laser is as low as $ 2 per unit Watts\textsuperscript{151}, this suggests that it is commercial viable to process materials with a high power laser system.

Not all oxides are detrimental to AM parts. Saeidi et al.\textsuperscript{152} and Rottger et al.\textsuperscript{153} found that the oxygen pickup during LAM and powder recycling promoted the formation of nano-size oxide of amorphous chromium silicate in SS316L. This compound led to a strong dislocation pinning effect which strengthened the mechanical properties of the AM part.\textsuperscript{152}

### 2.4.4 Effects of powder properties

Dawes et al.\textsuperscript{154} addressed a list of powder key process variables (KPVs) that influence the LAM process, see details in Table 2. In addition to the KPVs, the cost of the powder feedstock is also a part of the material selection process which indirectly affects the final properties of the LAM part.
Plasma rotating electrode (PREP), gas atomised (GA) and water atomised powders are commonly used in LAM. For example: the cost of PREP Ti-6Al-4V powder (US$ 185 - 416 per Kg) is more expensive than GA Ti-6Al-4V powder (US$ 161 – 260 per Kg)\textsuperscript{155} which is more expensive than water atomised Ti-6Al-4V powder (US$ 30 – 50 per Kg). To ensure LAM remains a cost-effective manufacturing process, it is important to address the impact of powder types on the LAM process.

Ahsan et al.\textsuperscript{156} reported that PREP and GA powders were spherical in shape; however, PREP powder exhibited three times less porosity than that of GA powder which exhibited an internal porosity of 0.017% and 0.055%, respectively. They also reported that the metal parts made by PREP powder showed less porosity than those produced by GA powder\textsuperscript{156}. However, the resultant porosity in the AM parts was found to be ca. 0.025%, suggesting that other defect formation mechanism was taking place during LAM, in addition to, a gas transfer from the powder to the AM parts.

Water atomised powder has an irregular shape and a relatively high oxygen content compared to that in PREP and GA powders.\textsuperscript{128,157} The disadvantage of using irregular shape powder particles is that they can mechanically interlock with each other and lead to powder bridging, causing a hindrance in the powder delivery process.\textsuperscript{71} During LAM, the molten pool produced by the water atomised powder showed a poor wetting behaviour which led to the formation of agglomerates and inter-agglomerate pores\textsuperscript{128}, lowering the part density.

Some studies suggested that powder with a poor flowability could introduce voids in the powder bed, reducing the powder packing density and effective thermal conductivity of the

<table>
<thead>
<tr>
<th>Particulate properties</th>
<th>Bulk properties</th>
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<tr>
<td>Particle size distribution</td>
<td>Apparent density</td>
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<tr>
<td>Particle shape (and morphology)</td>
<td>Tap density</td>
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<tr>
<td>Powder packing density</td>
<td>Flowability</td>
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<td></td>
<td>Chemical composition</td>
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<td>Optical properties</td>
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Table 2: Powder key process variables (modified after\textsuperscript{154})
powder bed\textsuperscript{55,148,158}. All of which can promote porosity formation during LAM\textsuperscript{159}. Several studies suggested that the flowability can be improved using spherical-like particles,\textsuperscript{159,160}, a wide PSD\textsuperscript{159}, or a very fine and narrow PSD.\textsuperscript{160} Seyda et al.\textsuperscript{159} showed that the PSD increases after 12 LAM production cycles, causing the surface roughness of as-built AM part to increase from 90 µm to 120 µm. In contrast, Gu et al.\textsuperscript{161} demonstrated that there are minimal differences in the effects of powder flowability on the LAM process, resultant density and mechanical properties of AM parts. Olakanmi\textsuperscript{148} demonstrates that powder agglomerates during powder blending, transportation, and storage reduces the packing density of the powder bed, and leads to defect formation. Perhaps, there is a critical powder flowability value for specific material that leads to poor packing density and defect formation which requires further studies to confirm that.

2.5 Powder materials

Powder materials can be made out of polymers\textsuperscript{162}, metals \textsuperscript{73}, alloys \textsuperscript{48}, ceramics \textsuperscript{163}, (or glass\textsuperscript{164}), and metal matrix composites (MMC)\textsuperscript{165}. Two classes of materials have been selected for this review: (1) Alloys (SS316L and Invar 36) and (2) glass, because they show great potential across a broad range of applications in our daily lives.

2.5.1 Stainless steel (SS316L)

Stainless steel (SS316L) is a Fe-based alloy, which has a typical composition of 16 – 18.5 wt% Cr, 10 – 14 wt% Ni, 2 – 3 wt% Mo, 2 wt% Mn, 1 wt% Si, 0.045 wt% P, 0.03 wt% C and balance Fe.\textsuperscript{166} It is commonly used in numerous sectors, including automotive, food processing, pharmaceuticals, marine, and general tooling, owing to its outstanding corrosion, oxidation and heat resistance as well as excellent mechanical properties. Several industries utilised the benefits of AM technologies and SS316L properties to produce energy storage\textsuperscript{15}, nuclear fusion\textsuperscript{167–169} and biomedical\textsuperscript{170,171} devices.

Porosity, cracking and surface roughness are known problems for SS316L AM applications. These defects act as crack initiation sites which are detrimental to the resistance to fatigue crack, however, the tensile behaviour of AM SS316L parts are comparable to wrought products.\textsuperscript{172} Studies have shown that the pore formation in SS316L was usually at the boundaries of the molten pool\textsuperscript{167,173} or at the interlayer binding sites\textsuperscript{174}. Over the past
decade, there were several hypotheses on pore formation, including insufficient laser melting\textsuperscript{167}, vaporisation of low boiling point elements, trapped gases (of Ar, CO or CO\textsubscript{2})\textsuperscript{123,166} from the powder, between melt tracks\textsuperscript{105}, or exsolution of dissolved gases during solidification.\textsuperscript{122,174} In addition, voids can be created by poor packing between a melted track and a new powder layer, and balling is thought to promote the formation of large irregular pores in subsequent layers.\textsuperscript{117,157} Morgan \textit{et al.}\textsuperscript{105} hypothesised that laser melting caused the trapped gas to expand rapidly while removing the liquid above it, resulting in an irregular pore\textsuperscript{105} or an open pore described by Qiu \textit{et al.}\textsuperscript{125}. These pores appeared as dents at the top surface of the AM parts, which increased their surface roughness. However, this theory is still insufficiently understood.

The effects of process parameters on the microstructure and mechanical performance of AM SS316L have been extensively investigated.\textsuperscript{115,117,126,153,157,170,174,175} Li \textit{et al.}\textsuperscript{167} summarised these research findings in short: Low $P$ with a high $v$, a high $t$ of $>50$ $\mu$m, and high oxygen (2 – 10 \% or $>100$ ppm) content on the powder or build chamber would yield poor wetting characteristics of the SS316L molten pool. Poor wetting leads to the formation of balling instead of a continuous track, resulting in a high volume of irregular porosity and poor mechanical performance.\textsuperscript{117,126,157} However, Wang \textit{et al.}\textsuperscript{174} successfully fabricated 99.99\% dense SS316L parts with a layer thickness of 150 $\mu$m, because they had better control over the laser scanning parameters using a modulated laser system. Kruth and Yasa\textsuperscript{166,173} demonstrated that laser surface re-melting (LSR) or laser re-melting can refine the grain structures, reduce surface roughness, porosity and residual stresses in SS316L. Alternatively, other studies suggested that an increase in the overlapping distance (40 – 50 \%) between melt tracks may also reduce balling and crack formation.\textsuperscript{157,174} Even so, the underlying mechanism for pore removal during laser re-melting is still insufficiently understood.

Kruth \textit{et al.}\textsuperscript{122} reported that rapid solidification prevented the formation of lath martensite and hence the resultant microstructure showed cellular columnar grains. These grains were usually tilted towards the building direction and perpendicular to the isotherms. Although the Hall-Petch relationship\textsuperscript{176} shows that the finer the grain size the better mechanical properties, studies reported that the excellent mechanical strength of AM SS316L was due to the intragranular cellular structure containing randomly distributed nano-size oxide inclusions\textsuperscript{169} of
amorphous chromium silicate. More detailed studies in these areas are needed to better understand the thermal history and solidification process to control the formation and evolution of such interesting microstructure.

2.5.2 Fe-Ni alloy

Fe-Ni alloy is also known as Invar alloy because it has a nearly zero and almost constant thermal coefficient of expansion (CTE) below its Curie temperature of 200 °C. The Invar alloy system shows excellent dimensional stability and mechanical properties in a cryogenic environment. With the additions of Cr, Cu, and Mo, the Fe-Ni alloy system exhibits excellent soft magnetic properties. To date, Invar alloys are currently being used in the applications of precision instruments, optical devices, electronic packaging, moulds and aircraft tooling.

Qiu et al. and Harrison et al. investigated the microstructure, CTE and mechanical properties of Invar 36 AM parts. They showed that the Invar 36 AM parts exhibited an epitaxial columnar grain structure, some of which had grown through several powder layers. These large columnar grains were found at the bottom of the component whereas a mixture of columnar and fine fan-like structures was found at the top of the sample (Figure 18). Qiu et al. identified that these grains were primarily made of $\gamma$-(Fe, Ni) with a small volume fraction of $\alpha$-Fe, which matched well with the phase diagram (Figure 19).

![Figure 18: SEM images showing the microstructures of an Invar 36 AM sample: a, an SEM image labelled with the inverse pole figure showing large columnar grains. BD/Z is the building](image-url)
direction and TD/X is the transverse direction. \( b \), an SEM image of fine fan-like grain structure near the top of the AM sample (after\(^{125}\)).

![Phase diagram of the Fe-Ni alloy system](image)

**Figure 19:** Phase diagram of the Fe-Ni alloy system (after\(^{179}\)). The purple dotted line possible phases presented during solidification of Invar 36 alloy. The green dotted line shows the Curie temperature with respect to the alloy composition.

Qiu *et al.*\(^{125}\) reported that open pores were found on the surface of AM parts. They hypothesised that the formation of open pores is linked to (1) an unstable fluid flow or (2) incomplete melting of powder particles due to a high \( v \). To suppress the development of porosity, they suggested that a high \( P \) could raise the temperature of the molten pool and allow the molten pool to wet and spread.

The mechanical properties of Invar 36 AM parts were comparable to that of cold drawn and superior to that of annealed parts.\(^{125,178}\) Harrison *et al.*\(^{178}\) demonstrated a stress relieved SLM Invar 36 sample had a much higher CTE than that of an as-built Invar 36 part. They suggested that the accumulation of residual stress in AM contributed to the reduction of CTE in the as-built Invar 36 part.\(^{178}\) The magneto-volume effect reduced the volume of the lattice structure with increasing temperature and compensated the CTE induced by lattice vibration. Therefore, Invar 36 maintained a low CTE until the material reached its Curie temperature.\(^{181}\)
The aforementioned studies mainly focused on the final properties of AM Invar 36 parts. However, there is insufficient understanding regarding the development of defects, especially on those spherical and open pores arise from the AM process, which is key to help users to select the optimised parameters for producing a high-quality AM part.

2.5.3 Glass

There has been increasing interest of using LAM technologies to produce biomedical components from bioactive glass\textsuperscript{164,182,183} and to fabricate transparent optics and glassware from soda-lime\textsuperscript{184–186}, borosilicate\textsuperscript{187} and silica glass\textsuperscript{185,188,189}. Similar to metal AM, process defects (\textit{e.g.} cracking\textsuperscript{189} and bubble entrapment) and detrimental residual stresses are major barriers to adopt LAM for making glass components.\textsuperscript{187} In addition, there are other challenges for glass AM, including the low absorption of visible light and near infra-red (NIR) in glass, low thermal shock resistance due to its high heat capacity,\textsuperscript{185} elastic modulus and coefficient of thermal expansion.\textsuperscript{189}

Kolan \textit{et al.}\textsuperscript{164,182,183} performed indirect SLS of 13-93 bioactive glass (premixed with a binder material of stearic acid) using a CO\textsubscript{2} laser. They emphasised that the 13-93 bioactive glass cannot be fabricated directly without a binder. However, Fateri \textit{et al.}\textsuperscript{184,185} and Luo \textit{et al.}\textsuperscript{186} successfully performed LAM of soda-lime glass (without a binder addition) using Yb: YAG-pulse and CO\textsubscript{2} lasers, respectively. None of the aforementioned studies have explained why a glass can be processed with or without binder materials, moreover, the laser-absorption mechanism in LAM of glass powders is not very clear.

Although employing a high preheating temperature has proven to reduce cracking and accumulation of residual stresses during LAM\textsuperscript{189,190} but it does not fully eliminate these issues. Bubble entrapment is an utmost concern in glass AM, because it causes optical scattering and limits the optical performance of glass. Luo \textit{et al.}\textsuperscript{186} addressed that bubble (air or gas) entrapment in the glass structure was linked to the high viscosity of glass but the underlying formation mechanisms of trapped bubbles have not been widely investigated. However, they identified three types of bubbles in the glass AM parts: periodic bubbles, sporadic bubbles, and foam layers.\textsuperscript{187} Periodic bubbles were usually found at the interface between the scanned tracks or layers. Sporadic bubbles were usually originated near the contamination or defects.
of the feedstock material. Foam layers were possibly caused by rapid exsolution of dissolved gases as a result of overheating the glass material during AM. This mechanism is also known as reboil in conventional glassmaking process.\textsuperscript{187} Furthermore, Khmyrov \textit{et al.}\textsuperscript{189} explained that overheating of glass could induce intensive vaporisation which could contribute to the formation of the deep groove at the glass substrate.

Similar to metal AM, Fateri \textit{et al.}\textsuperscript{184,185} found that that high LED can cause spheroidisation (or balling), bubble formation, deformation, and bulging. In contrast, a low LED would form weak bonding between particles, producing AM parts with poor mechanical properties and dimensional accuracy. With the aid of \textit{in situ} high-speed optical imaging, Zhirnov \textit{et al.}\textsuperscript{188} determined the principal consolidation phenomena of silica glass was by viscous merging. Similar to metal AM, there is little understanding regarding the laser-absorption, powder consolidation, and defect evolution mechanisms during glass AM.

\subsection*{2.6 \textit{Ex situ} characterisation}

Material characterisation plays a crucial role in developing our fundamental understanding of the process-microstructure-properties relationship in AM. Over the past three decades, the microstructure of AM samples had been studied by a range of microscopy techniques. Murr \textit{et al.}\textsuperscript{191} examined a range of AM materials using a combination of 3D light optical microscopy (LOM) and transmission electron microscope (TEM). These LOM and TEM images showed top, front and side views of the microstructure at a very high spatial resolution (< 200 nm), providing a semi-3D visualisation of the sample. Many research groups also used a combination of scanning electron microscopy (SEM) with Electron Back Scattered Diffraction (EBSD) and energy dispersive X-ray (EDX) spectroscopy to reveal the orientations, morphologies and chemical compositions of the AM grain structures (see \textbf{Figure 20}).\textsuperscript{192–194} Several studies had identified microstructure heterogeneities along the build height of the AM samples of Al\textsubscript{10}SiMg\textsubscript{67} Ti-6Al-V\textsuperscript{194} and Invar 36\textsuperscript{125}. Undoubtedly, the LOM, SEM and TEM images provided detailed information on the microstructural features across length scales from mm to nm. However, sample preparation required destroying a functional AM part, the captured images are limited to two dimensions and lack temporal information regarding the LAM process.
Figure 20: EBSD orientation maps for an AlSi10Mg SLM part: a, a side view of the EBSD map perpendicular to the building direction and b, a top view of the EBSD map along the scan and building directions. (after 67)

X-ray computed tomography (XCT) is an alternative ex situ characterisation technique that is non-destructively and provides detailed information in three-dimensions (3D). So far, users have employed XCT to quantify the surface roughness14 and dimensional accuracy of the AM parts22, in addition, sizes, shapes, and locations of the defects in the powder materials156 and AM parts195–198. Furthermore, Sercombe et al.199 and Zhang et al.200 combined XCT with finite element modeling or other modeling techniques to determine the failure behaviour and mechanical performance of the AM components. However, there are several disadvantages of using XCT for full production analysis in AM, including a limitation of X-ray penetration with high atomic number material (e.g. Fe); the analysis pipeline needs to be performed by highly-skilled workers, and hence it is a lengthy process to obtain results.
2.7 *In situ* characterisation

Many existing consolidation theories were developed based on post-mortem examinations which lacked time-dependent information. Given that the laser-material interaction, powder consolidation, and solidification occur so rapidly, the underlying physics behind these processes remains unclear. To address this knowledge gap, many research groups employed a range of *in situ* and real-time characterisation techniques to extract time-resolved information from the LAM process, including high-speed optical imaging, thermography and pyrometry, dynamic transmission electron microscopy and X-ray radiography. This section summarises the applications of these techniques on additive manufacturing.

2.7.1 High-speed optical imaging, thermography, and pyrometry

Song *et al.*\(^7\) reported the first real-time observations of particles melting, the formation of agglomerates (i.e. balling) and spatter at the laser-matter interaction zone using a high-speed video camera in a millisecond range.\(^7\) Similarly, Rombouts *et al.*\(^1\) employed a custom-built coaxial imaging system at 250 frames per second (fps) to capture the evolution of molten pool who also developed an automated image processing algorithm to extract the melt pool geometry, in terms of area, length \((l)\) and width \((w)\), see Figure 21. Kruth *et al.*\(^4\) implemented a closed feedback loop system based on Rombouts *et al.*\(^1\) coaxial setup which enabled autonomous control of the laser power to maintain the molten pool geometry at constant during AM. As a result of that, they made a significant improvement on the surface quality of the overhang structure.\(^4\) This system was further developed by Craeghs *et al.*\(^2\) who have mapped the molten pool data in space to facilitate detection of defects in an AM build.

![Figure 21](image)

*Figure 21:* Typical images of a molten pool captured by the K.U. Leuven coaxial setup: a, grey scale image and b, a processed image overlaid with a segmented molten pool (after\(^1\))

However, the measurement of the molten pool geometry may encounter errors for LAM of highly reflective metals, because the light reflections from the incandescent molten pool could saturate the detector of the camera. To address this issue, Lott *et al.*\(^2\) developed a separate
coaxial system coupled with an illumination source and a narrow band-pass filter that removed light emissions from the incandescent molten pool except for the wavelength of the illumination source. Several groups adopted a similar optic design proposed by Lott et al.\textsuperscript{203} and reported improvement on the overall image contrast.\textsuperscript{203–205}

Instead of using a coaxial system, several groups placed an optical imaging camera at an elevated angle from the powder bed surface. Furumoto \textit{et al.}\textsuperscript{205,206} and Alkhari \textit{et al.}\textsuperscript{207} used a high-speed camera with a two colour pyrometry to capture the changes in morphology and the surface temperature of the melt track. They highlighted that the changes in melt track morphology heavily depended on the surface tension and surface temperature of the melt track. In their studies, they concluded five possible line consolidation mechanisms in LAM (Figure 22). To study the powder consolidation mechanisms in a commercial AM process, Qiu \textit{et al.}\textsuperscript{22} integrated an optical imaging system (frame rate of 5 kfps) into a Concept Laser M2 Cusing SLM system. They revealed that the amount of material evaporation\textsuperscript{144}, spatter and track width increased with increasing $P$.\textsuperscript{22} However, they were unable to quantify the size, trajectories, and velocities of the spatter because the pixel resolution of the imaging system was 2 to 3 times larger than the powder size distribution.
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**Figure 22**: Five types of line consolidation mechanisms (after 207)

Matthews *et al.* 208 and Ly *et al.* 209 used a combination of a very high-speed imaging system (frame rate of 500 kfps) and a bespoke LPBF rig to reveal the underlying spatter phenomena during LAM under various argon gas pressures (**Figure 23**). Their key findings hypothesised that spatter was mainly caused by metal vapour-driven particle entrainment at a low gas pressure (*e.g.* < 10 Torr) (**Figure 23a**). At a high argon gas pressure, the inward argon gas flow either caused the entrained powder particles to incorporate into the melt track, spatter across the powder bed, or induced a further laser-spatter interaction that transformed the powder spatter into droplet spatter (**Figure 23b**). Bidare and Bitharas *et al.* 210 visualised and correlated the spatter behaviour with respect to the flow dynamic of the plume (which consists of metal vapour and plasma) using a bespoke LPBF rig together with high-speed optical and
Schlieren imaging. They confirmed that the fast-moving plume above the molten pool was the root cause of the inward argon flow. However, there are still no solutions to mitigate spatter during LAM.

Beside spatter, Trapp et al.\textsuperscript{66} used very high-speed imaging to observe the changes in the surface morphology of the melt tracks from depression to keyholes with increasing LED. Combined \textit{in situ} very high-speed imaging with a multi-physics model, Bertoli \textit{et al.}\textsuperscript{204} predicted that the cooling rate of the melt tracks ($\sim 10^6$ K/s) was inversely dependent on the input LED.

![Figure 23: Schematic of the spatter mechanisms: a, at a low gas pressure, powder spatter is mainly driven by the laser-induced recoil pressure and b, at a high gas pressure, the combination of the laser-induced vapour jet with the inward argon gas flow can cause: (1) entrained powder, (2) powder and (3) droplet spatter.](image)

In addition to high-speed optical imaging, Furumoto \textit{et al.}\textsuperscript{205,206}, Alkhari \textit{et al.}\textsuperscript{207} and Pavlov \textit{et al.}\textsuperscript{211} found that there was a strong positive correlation between the pyrometry signals and the resultant build features. The advantage of using a pyrometry technique is its fast response time (up to $10^{-6}$ s) however it is limited to a single temperature measurement over a large spot. The spot size depends on the instrument and its distance away from the object. Therefore, Bayle \textit{et al.}\textsuperscript{212} and Krauss \textit{et al.}\textsuperscript{213} used IR-thermography as a more advanced \textit{in situ} characterisation technique, because it provided a temperature distribution across the entire powder bed which can be used to correlate defect positions. This information can be fed into appropriate simulation models. Thermography has also been applied to many other AM processes which have been reviewed by reference studies.\textsuperscript{42,43} The current IR thermography technique is mainly limited by a low pixel resolution of 100 $\mu$m and a slow frame rate of 2000
fps owing to a low quantum efficiency for converting light (visible light to NIR regions) into digital images. Future improvements in the spatiotemporal resolution of the thermography setup would enable more detailed studies of the powder consolidation and solidification processes in LAM.

### 2.7.2 Dynamic transmission electron microscopy

To study high spatiotemporal resolution of ultra-fast material science, Lawrence Livermore National Laboratory developed a dynamic transmission electron microscopy (DTEM) technique that uses a Nd: YLF laser ($\lambda = 211$ nm) to generate a bunch of electrons for imaging or diffraction. The Nd: YLF laser is synchronised to a Nd: YAG laser ($\lambda = 1064$ nm) that drives a laser-sample interaction. The DTEM enables users to observe high quality, real-space images of material dynamics with a spatial resolution of 10 nm and a temporal resolution of 15 ns.\textsuperscript{214–218} Several authors demonstrated the applications of DTEM to study the rapid solidification behaviour (e.g. grain growth and phase transformation) of Ge\textsuperscript{218}, Al-Cu\textsuperscript{215} and Al-Si\textsuperscript{217} alloys during laser melting. However, the limitation of DTEM is the ability to move the laser source across the sample, therefore it could only study dynamic phenomena of a single molten pool.

### 2.7.3 X-ray radiography

The X-ray imaging setup consists of an X-ray source, a sample and an imaging system (Figure 24). The X-ray radiation can be generated using an X-ray tube or a synchrotron source. As the X-ray interacts with the sample material, some of the X-ray energy is being absorbed, scattered and transmitted, the imaging system converts the attenuated X-rays into a digital image or a projection via scintillation.

There are many important factors that affect the image quality which has been outlined by Stock\textsuperscript{219}. In order to visualise the small features within the sample, the image must have a high contrast ratio of the signal difference between the foreground ($signal_{foreground}$) and the background ($signal_{background}$) to the background signal, see expression in Equation 14:

$$\text{contrast} = \frac{|signal_{foreground} - signal_{background}|}{signal_{background}}$$  \hspace{1cm} \text{Equation 14}
The other important factor is the transmission to absorption ratio of the incoming X-ray, which can be calculated by the Beer-Lambert Law given in Equation 15:

\[
\frac{I}{I_0} = \exp\left[-\left(\frac{\mu}{\rho}\right)\rho x\right]
\]

**Equation 15**

where \(I_0\) is the intensity of the generated X-ray beam; \(I\) is the intensity of attenuated X-ray beam after it interacts with the sample with a thickness of \(x\) and density of \(\rho\). The linear attenuation coefficient \((\mu)\) depends on the energy of the X-ray beam and the atomic number of the element. Notably, the \((\frac{\mu}{\rho})\) is a normalised value for \(\mu\), also known as the mass attenuation coefficient. The purpose of the conversion is to produce a constant value of \(\mu\) for a particular substance.

![Figure 24](image1)

**Figure 24:** X-ray radiography apparatus to study melt pool dynamics in laser welding: a, a photograph and b, a sketch of the setup where the weld sample interacts with a laser beam while imaging by X-rays; c, a typical radiograph of a weld structure. (after 220)

The X-ray absorption of a given substance depends on the X-ray photon energy (Figure 25), the material absorbs more X-rays if it has a high atomic number (Z), hence the half thickness value of a high Z material (e.g. Fe) is always lower than that of a low Z material (e.g. Al) at all photon energies.

The use of X-ray radiography to study molten pool dynamics in laser processing is not new, and hence some of the experimental ideas are transferable to study LAM.220–226 Lee et al.221 observed the keyhole behaviour, melt flows, bubbles and porosity formation during laser welding of metals (Figure 26). Heider et al.220 used a series of X-ray radiographs to explain...
the bubble formation at the tip of the capillary, including melt ejection and pore formation. Boley et al.\textsuperscript{223} combined the X-ray radiographs, optical sectioning and high-speed optical images to reconstruct molten pool geometry in 3D (Figure 27).

Figure 25: The attenuation coefficient and half-thickness of Fe and Al over a range of photon energies (after \textsuperscript{222})

\[ P = 4.5 \text{ kW}; \nu = 55 \text{ mm s}^{-1}; \text{Gap} = 0 \text{ mm}, 1.4\text{mm}-1.2\text{mm}-0.65\text{mm} \]

Figure 26: A sequence of X-ray images showing the formation and evolution of a keyhole, bubbles, and porosity during laser lap welding of 3 metal sheets (after \textsuperscript{221})
Figure 27: Three-dimensions molten pool geometry: a, extracted information from imaging (blue), sectioning results (green) and a projection acquired from the X-ray imaging (orange). b, a reconstructed melt pool geometry in three-dimensions (after\textsuperscript{223})

Zhao et al.\textsuperscript{227} were first to report \textit{in situ} observations of defects (e.g. keyhole pores and spatter) and grain evolution during LPBF of a single molten pool. They demonstrated that time-resolved images could be used for quantification of the solidification rates during AM. However, there are still insufficient physical understanding regarding the evolution of defects inside melt tracks or the thermophysical interactions between two or more melt tracks.

Although X-ray imaging enables users to observe the dynamic behaviour during the laser-matter interaction and powder consolidation, its limitations are: (1) the radiograph integrates all information through the sample thickness, it also does not provide sufficient information about the (2) chemical composition and (3) thermal history of the processed materials.

In this section, the tremendous progress that has been made in LAM using a wide range of \textit{in situ} characterisation techniques was reviewed, uncovering new observations behind the thermophysical processes during LAM. Many of these techniques complement each other. The future research will combine these techniques together to study the laser-matter interaction, powder consolidation and solidification of powder particles in LAM.

\subsection*{2.8 Summary}

LAM is a versatile and disruptive technology in the manufacturing industry owing to its ability to produce parts with a high degree of design freedom and short lead time. This review highlights the current technological challenges in LAM regarding microstructural anisotropy,
defects, poor surface finish and undesired residual stresses. All of which have limited the applications of AM to non-safety critical components. These challenges could be overcame with improved understanding in the laser-matter interaction, powder consolidation, and solidification processes. The current literature addresses the effects of LAM process parameters and intrinsic material properties on the resultant microstructure and properties, however, the underlying formation mechanisms of defect and melt tracks as well as the molten pool dynamics in LAM remain unclear.

Even so, many powder consolidation and solidification theories were developed based on parametric studies using ex situ characterisation techniques and extended by in situ high-speed imaging, pyrometry, and IR thermography. These results were limited by capturing phenomena on the powder bed surface and could not elucidate the evolution of porosity and the complex fluid flow behaviour inside the molten pool.

The study of the molten pool dynamics in LAM is experimentally challenging, Zhao et al. in June 2017 were the first group to report on the molten pool dynamics of a single molten pool by X-ray radiography. To date, there are no other reports regarding the evolution of defects (e.g. porosity) during LAM of a full melt track or multiple layers of melt tracks. This emphasised that there is a need to further develop X-ray radiography or other advanced characterisation techniques to reveal the missing physical understanding in LAM. Most importantly, the aim of future studies should provide crucial data to validate existing theories on the laser-matter interaction, powder consolidation, and solidification, in addition to, verifying the predictions of molten pool behaviour from simulation tools.
Chapter 3:
A laser additive manufacturing process replicator (LAMPR) for real-time and *in operando* synchrotron X-ray radiography

*Note: a version of this chapter will be submitted to Additive Manufacturing: “A laser additive manufacturing process replicator (LAMPR) for real-time and in operando synchrotron X-ray radiography”, Leung et al. 2017*
Author contribution statement:

Chu Lun Alex Leung – Main investigator of this research who conceived the detailed ideas, co-designed and built the experimental apparatus, contributed to the synchrotron proposal, designed the experiments, performed all experiments apart from the production of 13-93 bioactive glass and XRF analysis. Analysed all the data, data interpretation and wrote the results in this chapter.

Sebastian Marussi and Michael Towrie – Co-designed and built the experimental apparatus and provided comments on data interpretation.

Jesus del Val Garcia – Produced the 13-93 bioactive glass and also performed SEM and XRF characterisation on 13-93 bioactive glass.

Robert C. Atwood and Andrew J. Bodey – Support in two separate beamline experiments, also provided comments on results and discussion.

Julian R. Jones – Contributed to the bioactive glass experimental design, comments on data interpretation, results, and discussion.

Philip J. Withers - Contributed to the synchrotron proposal, provided comments on the data interpretation, results, and discussion.

Peter D. Lee – Conceived the overall project idea, contributed to the synchrotron proposal and provided comments on data interpretation, results and discussion.
Abstract

Laser-matter interactions are fundamental to laser additive manufacturing (LAM). These phenomena occur on short time scales ($10^{-6}$ - $10^{-3}$ s) and have proven difficult to characterise. We study these interactions during LAM of stainless steel (SS316L) and 13-93 bioactive glass powders using a custom built LAM process replicator (LAMPR) with *in situ* and *operando* synchrotron X-ray radiography. The time-series radiographs reveal the distinct evolution of melt tracks, spatter and porosity. It also demonstrates the differences and similarities between LAM of SS316L and a 13-93 bioactive glass owing to the variance in their chemical, optical and thermophysical properties. The steel absorbs the laser power at its surface while trace elements in the bioactive glass are responsible for absorbing laser power within the particles. Our results confirm that a low viscosity melt, e.g. SS316L, tends to: generate spatter; form melt tracks by molten pool wetting; promote pore migration; and release entrained gas pores into the atmosphere. In contrast, a high viscosity melt, e.g. 13-93 bioactive glass, tends to: inhibit spatter formation by damping the Marangoni convection; and form melt tracks by viscous flow, which also facilitates pore formation and growth. In addition to revealing new mechanisms, we also quantified spatter velocities, molten pool geometries (length and depth) and melt track shrinkage (%) over time; which can be used to validate and improve existing simulation tools.
3.1 Introduction

Laser additive manufacturing (LAM) technologies fuse powder material together using a focused laser beam to build up a three-dimensional object, that can have complex features, layer upon layer. LAM technologies are also referred to as selective laser sintering (SLS)\textsuperscript{47}, selective laser melting (SLM)\textsuperscript{228}, laser powder bed fusion (LPBF) and direct energy deposition (DED)\textsuperscript{6}. They bring new design paradigms and product applications across many different sectors, including nuclear fusion\textsuperscript{167}, aerospace\textsuperscript{13,17} and tissue engineering\textsuperscript{229,230}.

An entry-level LPBF system consists of a laser system, a powder reservoir and a build chamber that operates in an inert atmosphere (Figure 28). It has the ability to produce overhang and layer wise additive manufacturing (AM) builds. Overhang configuration describes the conditions when powder particles are fused together above loose powder instead of on a solid substrate.

![Figure 28: Schematic of a typical LPBF machine. The build chamber is purged with a flowing inert atmosphere, where the blue arrows indicate the gas flow direction.](Image)

While the potential of LAM is great, the adoption of such technologies for high-performance structural applications is hindered by many technical challenges, including the control of defects\textsuperscript{58,184,185} (e.g. porosity\textsuperscript{22,118,195}), non-uniform shrinkage\textsuperscript{10}, poor dimensional
accuracy$^{14,22,199}$, and surface quality$^{14}$. These challenges have led to inconsistent mechanical behaviour of LAM components during service$^{11,31,231}$. LAM begins with an interaction between a laser beam and powder particles, followed by a series of complex powder consolidation phenomena that occur on very short time scales ($10^{-6} - 10^{-3}$ s)$^{108}$. These phenomena cannot be studied by ex situ characterisation techniques, and hence they are currently not well understood.$^{42}$ Since the laser-matter interaction and powder consolidation are fundamental to microstructure and thereby the performance, a better understanding of such interactions is required.$^{35}$

In recent years, our understanding of AM has improved through ex situ destructive, e.g. metallography$^{191,232,233}$ and non-destructive, e.g. X-ray computed tomography (XCT)$^{14,22,195,199}$, techniques. The new understandings gained were validated and extended by a variety of in situ monitoring measurements$^{43}$, including high-speed videography$^{41,142,205}$, infrared (IR) thermography$^{67,205,207,212}$, pyrometry$^{206,212}$ and electron microscopy$^{216}$. However, these in situ techniques can only capture the temperature field and/or images at the molten pool surface but are unable to study the changes within the melt zone, e.g. fluid dynamics and evolution of defects.

With advancements in third-generation synchrotron radiation sources and free-electron lasers,$^{234}$ it is now possible to use a high flux X-ray beam to capture these dynamic processes radiographically at a high spatial resolution (a few micrometres) and high temporal resolution (microseconds to milliseconds)$^{235}$. High frame rate radiography has been used to study metal foaming$^{236}$, casting$^{237,238}$, laser welding$^{225}$ and LPBF$^{227}$, providing new knowledge of real-time kinetics, thermodynamics, phase transformations and transport mechanisms behind these processing technologies.

Here we describe a LAM Process Replicator (LAMPR) and its application on two high-speed X-ray imaging beamlines at the Diamond Light Source (DLS), UK, to study the laser-matter interaction and powder consolidation phenomena during LAM of stainless steel (SS316L) and bioactive glass (13-93). Our findings presented here shed new light on the effects of chemical, optical and thermophysical properties on the evolution of melt tracks, spatter and porosity, thus helping to explain and refine existing hypotheses in the literature.
Most importantly, we demonstrate that the understanding of laser-matter interaction is interchangeable across different classes of materials (e.g. alloys and glass), which is crucial for future materials development for LAM.

3.2 Methods

3.2.1 Technical description of the LAMPR

The Laser Additive Manufacturing Process Replicator is designed to emulate major functions of the LPBF system (Figure 28) while permitting in situ and operando imaging of the laser-matter interaction and powder consolidation phenomena with synchrotron X-rays. It is a compact, lightweight (~15 kg) and portable device that can be integrated onto different synchrotron X-ray imaging beamlines (Figure 29a). It consists of three sub-assemblies coloured differently in Figure 29a: 1) a stainless steel environmental build chamber (blue), 2) a laser system (green) and 3) a laser enclosure system (black). The environmental build chamber and the laser enclosure are each equipped with two circular boron nitride (BN) X-ray transparent windows (10 mm in diameter and 0.25 mm thick) to permit X-ray to pass through, see Figure 29a. This gives LAMPR a field of view (FOV) sufficient to capture the melt track evolution (with a minimum track length of 4 mm) in steady and non-steady states. For an overhang build configuration, a powder bed (30 mm long, 3 mm deep and 0.3 mm thick) is made from three BN plates (0.3 mm thick) stacked next to each other, in which the middle plate is 3 mm shorter in height than the others. For a layer-by-layer AM build, the middle plate is replaced by a metal substrate with a suitable height to match the thickness of a single powder layer.

Boron nitride is well suited for high temperature and X-ray imaging applications. It was used for all the LAMPR’s components along the X-ray beam path are made out of BN (giving a total material thickness of 1.6 mm). This gives an overall X-ray transmission of > 90% between 20 – 150 keV, providing an excellent image contrast of the sample materials. Furthermore, BN is not wet by most molten metals or slag, i.e. glass, allowing reuse of the sample holder. Alternatively, glassy carbon and Kapton™ may be used due to their low x-ray absorption and amorphous structures, which make them well suited for both X-ray imaging and diffraction studies.227
The sample is placed into the environmental build chamber via the side port (Figure 29b). This is designed for precision alignment of the powder bed to the focal position of the laser beam, and to be perpendicular to the X-ray beam. All the connected components are either sealed with O-rings or standard vacuum flanges, thus enabling the environmental build chamber to maintain a vacuum pressure of $10^{-3}$ Torr or support different gas flow environments at a pressure of 760 Torr. The IR window is made out of CaF$_2$ which has a high transmission percentage of 95 % across a wavelength of 0.3 – 6 µm. This enables LAMPR to perform correlative optical imaging and thermography at the powder bed surface while imaging the internal structure of the melt track during LAM.

The laser system consists of a ytterbium-doped fibre laser (wavelength of 1070 nm, transverse mode TEM$_{00}$, continuous-wave (CW), beam quality factor $M^2$ of 1.03, power ($P$) of 200 W (SPI Lasers Ltd, UK)), a beam expander, IR reflective optics and a Class 1 laser safety enclosure (complies with EN60825). The diameter of the collimated laser beam is increased from 5 to 10 mm via a beam expander before entering into an X-Y galvanometer (Laser control systems Ltd., UK). The X-Y galvanometer is capable of moving the 200 W laser beam at a scan velocity ($v$) up to 4 m/s. Lastly, the laser beam is focused down to a 50 µm diameter spot at a focal distance of 254 mm (or at the powder bed surface) via an f-theta lens and an IR reflector. The LAMPR is synchronised with the image acquisition system in synchrotron beamlines allowing in situ and operando synchrotron imaging in real and reciprocal space. In this study, we report the synchrotron X-ray imaging of stainless steel and a bioactive glass in LAM.
Figure 29: a, Schematic of LAMPR mounted on a synchrotron beam line. b, A three-quarter section view of the environmental chamber. The purple arrows indicate the directions of the incoming X-ray beam (dark purple) and the attenuated X-ray beam (light purple). The red arrow highlights the scan direction of the laser beam, which moves leftwards across the powder bed and the blue arrow indicates the argon flow direction.

3.2.2 Materials

In order to gain insight into the effects of powder properties on laser absorption mechanisms, melt flow behaviour and the evolution of the melt track and defects (e.g. spatter...
and porosity), we chose to examine the behaviour of two powders having large differences in chemical, optical and thermophysical properties. The two powders were: (1) a gas atomised stainless steel (SS316L) powder (Sandvik Osprey Ltd, Sweden) and (2) a melt-quenched bioactive glass (13-93) powder (54.6 mol% SiO$_2$, 22.4 mol% CaO, 6 mol% Na$_2$O, 1.7 mol% P$_2$O$_5$, 7.9 mol% K$_2$O, 7.7. mol% MgO).

They were chosen owing to their large differences in chemical, optical and thermophysical properties. SS316L has a near-infrared (NIR) absorption of 64 - 68 %,\textsuperscript{65,241} a melt viscosity of 8 mPa S at its melting temperature, and a freezing range of 1658 – 1723 K\textsuperscript{137}. Unlike SS316L, the 13-93 bioactive glass has a large sintering range between the glass transition and crystallisation onset temperatures (873 – 963 K)\textsuperscript{242}, and a melt viscosity of 2 Pa S at 1573 K.\textsuperscript{243} Studying their laser-matter interaction and consolidation phenomena will provide some basic understanding on the effects of powder properties, \textit{e.g.} viscosity, on the laser absorption mechanism, melt flow behaviour and evolution of melt track and defects (\textit{e.g.} spatter and porosity).

The 13-93 bioactive glass was fabricated using a melt quenching route described in reference studies\textsuperscript{244–246}. Precursors of SiO$_2$ (Prince Minerals, Stoke-on-Trent), MgCO$_3$, P$_2$O$_5$, CaCO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$, all with a purity > 96\% (Sigma-Aldrich, UK), were mixed together using a Wheaton bench-top small bottle roller for 3 h to ensure homogeneity. The mixture of oxides and carbonates was melted at 1400°C in a platinum (Pt/Au 95/5) crucible for 90 min and quenched in deionized water. The frit was dried at 120 °C for 24 h, and ball milled for 30 minutes at 500 rpm (Premium Line 7 ball mill, Fritsch GmbH, Germany). Finally, the powder was sieved for 60 min at 2 mm of amplitude (Vibratory Sieve Shaker Analysette 3 Pro, Fritsch GmbH, Germany) to discard any particles with a diameter greater than 150 μm.

The powder morphology was characterised by scanning electron microscopy (SEM, JEOL JSM-6610LV, Japan). The particle size distribution (PSD) of both powders was determined from the SEM images using the segmentation and object identification routines in the Image Processing Toolbox in MATLAB 2016a (Mathworks, USA). The SS316L composition was examined by Energy-Dispersive Spectroscopy (EDS). The 13-93 bioactive glass composition was characterised by inductively coupled plasma optical emission spectroscopy (ICP-OES,
Optima 4300 DV, Perkin Elmer, USA) following lithium metaborate fusion. After ball milling, we performed X-ray Fluorescence (XRF) to determine the impurity profile of the 13-93 bioactive glass. The diffuse reflectance (%) of the 13-93 bioactive glass was measured by UV-VIS spectrophotometer with an integrating sphere attachment (UV-2600 and IRS-2600 plus, Shimadzu Corporation, Japan). The spectrum was calibrated using a white standard of barium sulphate. The Kubelka-Munk function, $F(R)$, is often used to correlate the diffuse reflectance ($R$) to the absorbance of the 13-93 bioactive glass.\(^{247}\) The $F(R)$ is a ratio of the absorption coefficient ($K$) and scattering coefficient ($S$) of the powder as given in equation (16):

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$

(16)

3.2.3 In situ and operando synchrotron X-ray radiography setup

To observe the laser-matter interaction and powder consolidation process, we mounted the LAMPR on the hard X-ray beamline I12: JEEP to study LAM of SS316L and the medium energy X-ray Diamond-Manchester branchline I13-2 to study LAM of 13-93 bioactive glass, using the imaging parameters summarised in Table 3. Both beamlines are at the Diamond Light Source, UK.

Both experiments were performed under overhang configurations (Figure 28). A laser beam scanned a 4 mm line across the powder bed of SS316L (with a nominal $P = 150$ W and $v = 5$ mm/s) and 13-93 bioactive glass (with a nominal $P = 20$ W and $v = 5$ mm/s) in an argon atmosphere at a flow rate of 4 l/min. The $v$ was set to enable the formation of a continuous track under overhang configuration. The image acquisition system was synchronised with the LAMPR using a ring buffer mode that continuously recorded images into the on-board memory of the camera until the laser was triggered. Before the laser trigger point, 100 images were recorded as flat field images, and then a further 100 dark field images were taken without switching on the X-ray beam. These two sets of images were taken for flat field correction to remove image artefacts caused by pixel variations and thermal counts during image acquisition. Once the laser was triggered, a series of radiographs were captured at 5100 fps and converted into digital images via a 700 μm thick LuAg: Ce scintillator.
3.2.4 X-ray computed tomography (XCT)

After the in situ radiography experiments, both melt tracks were imaged topographically by using a Nikon XTH 225 X-ray tomography system (Nikon, Japan), see the acquisition parameters in Table 4. After image acquisition, we applied built-in beam hardening correction and filtered back projection algorithms in CT Pro3D (Nikon, Japan) to reconstruct a 3D image volume.

Table 3: Key characteristics of the synchrotron X-ray imaging systems used for this study at DLS.

<table>
<thead>
<tr>
<th>Beamline</th>
<th>I12: JEEP</th>
<th>I13-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy range (keV)</td>
<td>55 (Monochromatic)</td>
<td>14–25 (Pink)</td>
</tr>
<tr>
<td>CCD camera</td>
<td>Miro 310 M (Vision Research Inc., USA)</td>
<td>PCO.dimax S4 (PCO Group GmbH, Germany)</td>
</tr>
<tr>
<td>Sensor size (pixels)</td>
<td>1280 x 800</td>
<td>2016 x 2016</td>
</tr>
<tr>
<td>Bit depth</td>
<td>12 bit</td>
<td>12 bit</td>
</tr>
<tr>
<td>Field of view (mm)</td>
<td>8.4 x 3.3 (Region of Interest mode)</td>
<td>6.5 x 2.5 (Region of Interest mode)</td>
</tr>
<tr>
<td>Effective pixel size (µm)</td>
<td>6.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Acquisition speed (fps)</td>
<td>5100</td>
<td>5100</td>
</tr>
</tbody>
</table>

Table 4: XCT acquisition parameters for the imaging of SS316L and 13-93 bioactive glass melt tracks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Accelerating voltage (kV)</th>
<th>Beam current (µA)</th>
<th>Number of projections</th>
<th>Exposure time (ms)</th>
<th>Scan volume (mm³)</th>
<th>Voxel size (µm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS316L</td>
<td>100</td>
<td>80</td>
<td>3142</td>
<td>500</td>
<td>5.4</td>
<td>2.7</td>
</tr>
<tr>
<td>13-93 bioactive glass</td>
<td>50</td>
<td>130</td>
<td>3142</td>
<td>500</td>
<td>5.4</td>
<td>2.7</td>
</tr>
</tbody>
</table>
3.2.5 Image processing and quantification

The acquired radiographs were analysed using MATLAB 2016a. Firstly, they were normalized by flat-field correction (FFC) using the following equation:

\[ n = \frac{I_0 - \text{Dark}_{\text{avg}}}{\text{Flat}_{\text{avg}} - \text{Dark}_{\text{avg}}} \]

where \( n \) is the normalised image, \( I_0 \) is the raw image, \( \text{Flat}_{\text{avg}} \) is the average of 100 flat-field images, and \( \text{Dark}_{\text{avg}} \) is the average of 100 dark-field images. The FFC removed image artefacts that were introduced by pixel variations and thermal counts during image acquisition. Secondly, we applied a denoising algorithm, VBM3D\textsuperscript{248}, on these normalised images, followed by a custom background subtraction to improve their image quality for segmentation. After that, we extracted relevant melt features, and subsequently quantified the melt track geometry (e.g. length, width, and area) using standard MATLAB built-in functions. The area shrinkage (%) of the molten pool was calculated based on the (maximum molten pool area at the onset of the cooling stage – molten pool area after cooling) divided by the maximum pool area x 100 %.

For the SS316L dataset, we also tracked the spatter objects using the Manual Tracking plugin from ImageJ\textsuperscript{249} and subsequently calculated the spatter velocities. A detailed image processing flow chart and the resultant processed images are shown in Appendix Figure 2 and Appendix Figure 3, respectively.

The X-ray tomographs of the melt tracks were analysed using Avizo 9.1 (Thermo Fisher Scientific, US) to quantify their pore size distributions using the method described in ref\textsuperscript{14,250}. We discarded objects with less than five voxels (or an equivalent diameter of 6.75 µm) to minimize quantification errors induced by image noise.

3.3 Results

3.3.1 Powder characterisation

Figure 30 shows the powder characteristics of SS316L and 13-93 bioactive glass. The SS316L powder particles were mostly spherical though some were slightly elongated (Figure 30a) whereas the shape of the 13-93 powder particles were mostly irregular (Figure 30b). The PSDs for SS316L and 13-93 bioactive glass were 30 - 105 µm and 5 - 140 µm, respectively (Figure 30c).
The EDX analysis results (Table 5) detected up to 2.5 wt% of oxygen from the SS316L powder. Nyborg et al.\textsuperscript{251} and Hedberg et al.\textsuperscript{252} revealed that the SS316L powder consisted of a mixture of Cr, Mn and Fe oxides that were formed during atomisation. The composition of the 13-93 bioactive glass was measured by ICP-OES (Table 6). After ball milling, the 13-93 bioactive glass was exanubed by XRF and found that it contained a small amount of impurities of Fe$_2$O$_3$, Al$_2$O$_3$, TiO$_2$, and SiO$_3$. The $F(R)$ of 13-93 bioactive glass (Figure 30d) indicates that the powder had the highest absorbance at 1130 nm and a relatively high absorbance at the laser wavelength.

**Figure 30:** SEM images of a, SS316L metallic powder and b, 13-93 bioactive glass powder. c, Particle size distributions. (d) Diffuse reflectance of 13-93 bioactive glass powder in Kubelka-Munk unit. The red region indicates the laser wavelength.
Table 5: Elemental compositions of the SS316L powder by EDX

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>O</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>Co</th>
<th>Nb</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64.3 ± 0.4</td>
<td>17.4 ± 0.2</td>
<td>11.4 ± 0.2</td>
<td>2.5 ± 0.2</td>
<td>2.1 ± 0.8</td>
<td>0.8 ± 0.7</td>
<td>0.4 ± 0.2</td>
<td>0.2 ± 0.2</td>
<td>0.1 ± 0.2</td>
<td>0.1 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Chemical compositions of the 13-93 bioactive glass by ICP-OES

<table>
<thead>
<tr>
<th>Method</th>
<th>SiO2</th>
<th>CaO</th>
<th>K2O</th>
<th>MgO</th>
<th>Na2O</th>
<th>P2O5</th>
<th>Al2O3</th>
<th>SO3</th>
<th>TiO2</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP</td>
<td>53.0</td>
<td>20.0</td>
<td>12.0</td>
<td>5.0</td>
<td>6.0</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XRF</td>
<td>50.1</td>
<td>22.7</td>
<td>10.6</td>
<td>5.0</td>
<td>6.2</td>
<td>5.0</td>
<td>0.19</td>
<td>0.07</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3.3.2 *In situ* observation of LAM deposition of a SS316L track

A montage of time-series radiographs show the evolution of SS316L melt features from a crosssectional view of the powder bed during LAM (*Figure 31*). At the onset of LAM, the laser beam scanned leftwards across the powder bed, forming a molten pool at the right-hand side of the powder bed. The molten pool grew rapidly into a sphere; however, its growth rate slowed substantially as it reached a diameter of 500 μm (at 22 ms). At 63 ms, the laser scan speed surpassed the growth rate of the initial melt bead such that the laser beam formed a new molten pool 50 μm ahead of the first melt bead. At 146 ms, the new molten pool could be seen to coalesce with the previous melt bead to form a melt track. By 280 ms, more molten pools had formed and subsequently coalesced into large molten pools (*green circle*) along the scan path. By 350 ms, these large molten pools merged with the main melt track (*green circle*) and extended the track length. At 518 ms, no more molten pool wetting was evident and the melt track began to cool and shrink.

At the onset of LAM, it was evident that the molten pool rose ca. 50 μm above the powder layer possibly due to: (1) the molten pool’s geometry was larger than the width of the powder bed, and thus the molten pool was trapped between the BN plates; (2) the intense laser beam with a laser power density of > 10^6 W/cm² had caused metal vaporisation at the melt surface,
generating a recoil pressure at the laser-matter interaction zone. Since the melt track was built in an overhang condition, the recoil pressure forced the melt track to extend towards the bottom of the powder bed while forming spatter surrounding the melt track; unlike LAM on a solid substrate, the recoil pressure flattens the melt track or molten pool.\textsuperscript{253} We also hypothesised that the surrounding argon gas was heated by the metal vapours via heat conduction, expanding the gas/vapour jet outwards at high speed, generating forces to lift the molten pool away from the powder layer.

In some cases, these lift forces were sufficient to induce powder and droplet spatter (blue dotted circles at 63 and 146 ms), forming a denuded zone. We have successfully tracked 13 spatter during LAM and quantified the average and maximum spatter velocities, they were 0.16 m/s and 0.26 m/s, respectively. The radiographs indicate that the spatter trajectories strongly depended on the direction of the gas flow and the scanning laser beam. Since spatter and metal vaporisation removed material from the laser-matter interaction zone, this enlarged the denuded zone. Concurrently, powder particles consolidated into a molten pool or melt track. As a consequence, there was insufficient powder available along the scan path for track growth. Hence, the growth rate of the molten pool slowed down substantially.

During LAM, it was likely that the temperature at the centre of the molten pool was much higher than that at the edges of the molten pool. This developed a thermal gradient across the molten pool surface. The fluid moved away from the centre of the molten pool (a low surface tension region) to the edges of the molten pool (a high surface tension region), inducing a Marangoni-driven melt flow. When new molten pools formed ahead of the melt track, the resulting Marangoni-driven forces caused them to migrate opposite to the scan direction of the laser beam, facilitating molten pool wetting onto the melt track (Green dotted circle, Figure 31). These observations suggest that molten pool wetting was the primary track formation and growth mechanisms for SS316L.
Figure 31: A selection of time-series showing the evolution of a SS316L laser additive manufactured melt track ($P = 150$ W and $v = 5$ mm/s). Vertical red lines indicate the positions of the laser beam as it moves from right to left at different time points (red arrow). Blue arrow indicates the argon gas flow direction. Red boundaries show the outlines of the tracked objects. Blue circles highlight movement of the droplet spatter. Green circles show the track growth via molten pool wetting.

3.3.3 *In situ* observations of LAM of 13-93 bioactive glass track

A montage of time-series radiographs show the evolution of 13-93 bioactive glass during LAM (Figure 32). At 8 ms, the laser beam fused the glass powder into a molten glass bead at the right-hand side of the powder bed. At 22 ms, the molten glass bead grew larger while spherical gas pores with an equivalent diameter of 50 μm formed inside the glass bead. By 30 ms, some gas pores inside these glass beads had grown at the expense of others via pore coalescence. At 60 ms, the newly formed glass bead evolved rapidly into a 700 μm bead by merging with neighbouring glass beads or powder particles via viscous flow or viscous merging. At the same time, the first melt bead stopped growing and resided at the top of the powder bed. After that, glass beads and their internal pores continued to grow. At 92 ms, these gas pores inside the glass bead developed into a large gas pore with a diameter of 600 μm (blue arrow) which dramatically increased the volume of the glass bead. At 124 ms, the large gas pore burst open. Unexpectedly, the molten bead remained the same size and its internal structure retained many spherical pores. During 124 - 132 ms, these internal pores continued to coalesce and merge into larger pores; however, some of them had stopped growing.
From 108 ms onwards, it was evident that a glassy film formed a bridge between the second and third melt beads (green dotted line). At 142 ms, another glassy film appeared. It wrapped around the bottom sphere and connected with the two adjacent spheres. From 142 – 180 ms, this glassy film continued to pull the bottom sphere upwards (green arrows), enabling these spheres to make contact with each other. At 180 ms, necks formed between these spheres (red lines) and the glassy film became a part of the continuous glass track. Between 180 – 220 ms, the molten glass flowed slowly towards the contact regions from the left, promoting neck growth. The driving force for neck growth was to reduce the curvature of the neck surfaces and minimise the Gibbs free energy of the system. These observations confirmed that viscous flow was the main track formation mechanism for 13-93 bioactive glass.

**Figure 32:** A selection of time-series radiographs showing the evolution of a laser additive manufactured 13-93 bioactive glass track (\( P = 20 \) W and \( v = 5 \) mm/s). Vertical red lines indicate the laser beam positions. Blue arrows indicate the high-pressure gas pore. Green dotted boundaries highlight the glassy film and green arrows highlight the movement of the bottom glass sphere. Dark red lines show the necks between three spheres. Orange dotted circles highlight those pores that stop growing after pore coalescence.
3.3.4 Time-resolved quantification of SS316L and 13-93 bioactive glass melt tracks

The in situ observations show the dynamic changes of melt features during LAM, including the formation of melt tracks, denuded zones, pores and spatter. Using these radiographs, we have quantified the changes in the geometry and area shrinkage (%) of both melt tracks during LAM (see Figure 33).

The track length of the SS316L sample was 4.58 mm, ca. 15% larger than the nominal scan length of 4 mm (Figure 33a). The heat affected zone is always larger than the laser spot size, the melt track is expected to be longer than the nominal scan length, in addition, there is a possibility that the molten pool was constrained by the BN plates, squeezing it radially outwards. The track length of the bioactive glass was 2.8 mm, ca. 40 % shorter than the nominal track length, because the glassy film at the front-end of the track broke apart during sample handling, and thus the front-end of the track was excluded in the quantification. Figure 33b shows that the SS316L and 13-93 bioactive glass underwent a maximum shrinkage of 6.4 % and 3.2 % during LAM, respectively. The coefficient of expansion (CTE) of SS316L is $19.5 \times 10^{-6}$/K at 200 - 1000°C \(^{255}\), whereas the CTE of 13-93 bioactive glass is ca. $12.5 \times 10^{-6}$/K at the glass transition temperature of ca. 600°C \(^{256}\), in accordance with our results which show that SS316L contracted 50 % more than the 13-93 bioactive glass.

![Figure 33: Time-resolved quantification of a, molten pool geometry and b, area shrinkage (%)](image-url)
3.3.5 *Ex situ* analysis by XCT

The drawback of 2D radiographic imaging is that the melt features are overlaid with each other along the X-ray beam path, hence it is difficult to interpret whether these pores are opened or closed. In order to better understand the evolution mechanism of these pores, we conducted XCT analysis to reveal the internal structure of both melt tracks and provide measurements of their pore size distributions in 3D; see details in Figure 34a-c.

The overall porosity of the SS316L melt track is 0.03%, it indicates that the LAMPR is capable of producing a $>$ 99.9 % dense melt track under the overhang configuration. Of the porosity, 20% is closed pores with an average equivalent diameter ($D_{\text{avg}}$) of 10 μm, and the largest closed pore has a $D_{\text{avg}}$ of 27 μm. These closed pores in SS316L are likely to be gas pores owing to their spherical shape (Figure 34a) and small size (Figure 34c).

The 13-93 bioactive glass track has a porosity of 17.60 %, which is 500 times greater than that for SS316L, see Figure 34b and Figure 34c. Of the porosity, 18% of that is closed pores with spherical shapes however their $D_{\text{avg}}$ is 261 μm. Further, the largest open pore in 13-93 bioactive glass track has a $D_{\text{avg}}$ of 529 μm whereas the largest open pore in SS316L has a $D_{\text{avg}}$ of 83 μm. The 13-93 bioactive glass track exhibited pores with a diameter at least 5 to 10 times larger than those in SS316L, suggesting a different pore evolution mechanism involved during LAM of 13-93 bioactive glass compared to that involved in LAM of SS316L.
Figure 34: XCT porosity analysis of SS316L and 13-93 bioactive glass melt tracks. 3D surface rendered images of a, SS316L and b, 13-93 bioactive glass melt tracks. Both tracks are overlaid with closed pores (green) and open pores (yellow). c, Pore size distributions for both melt tracks.
3.4 Discussion

3.4.1 Laser absorption mechanisms

This study reveals two very different melt behaviours of SS316L and 13-93 bioactive glass during LAM. At the onset of the laser-matter interaction, the SS316L powder can absorb up to 68% of the incoming laser energy at a wavelength of 1000 nm via electron-electron and electron-photon interactions which then transfers the heat energy across the powder bed via heat conduction. The presence of surface oxides has not affected the molten pool dynamics during LAM of SS316L.

In theory, the major constituents of 13-93 bioactive glass, including SiO$_2$, MgO$^{257}$ and P$_2$O$_5$$^{258}$, have a minimal NIR absorption (< 5%). However, the reflectance measurement of the 13-93 bioactive glass shows 87.5% at the laser wavelength of 1070 nm, suggesting the absorbance of 13-93 bioactive is higher than expected. We postulate that was due to the presence of transition metal oxides (TMOs), such as TiO$_2$ and Fe$_2$O$_3$. The TMOs absorb the incoming IR radiation, re-emit some of the IR energy and promote powder melting. This is also known as the radiation conduction mechanism.$^{63}$ In addition, we also hypothesise that the multiple reflections (or scattering) of IR radiations increase the probability of laser absorption in the powder. The combined effects of radiation conduction and multiple IR reflections trigger the melting of 13-93 bioactive glass.

3.4.2 Melt track evolution mechanisms

As it can be seen in Figure 31 and Figure 32, the melt track formation of SS316L is primarily driven by molten pool wetting, whereas the melt track formation of 13-93 bioactive glass is driven by viscous flow (or viscous merging$^{188}$). As the laser beam scans across the SS316L molten pool, the Marangoni-driven flow causes the molten pool to move opposite to the scan direction of the laser beam, and then it coalesces onto the solidified beads, forming a melt track.

In contrast, the 13-93 bioactive glass undergoes viscous flow when the temperature is raised above its glass transition temperature of $\sim 600^\circ$C.$^{100}$ Notably, its flow behaviour is less viscous than traditional glasses due to its low content of SiO$_2$ and high content of alkali and
alkali-earth cations (e.g. K⁺ and Ca²⁺). The viscous flow behaviour is the driving force for the melt track formation of 13-93 bioactive glass.

3.4.3 Pore evolution mechanisms

Figure 34 shows that both melt tracks contained spherical gas pores. In general, the pore formation can be formed by an exsolution of dissolved gases, e.g. hydrogen, from a gas transfer from the powder particles, adsorbed moisture on the powder surface or the environmental build chamber. In the 13-93 bioactive glass study, we hypothesise that the laser-glass powder interaction was sufficient to generate low boiling point volatiles (e.g. Na, K, and Mg) from the molten glass, promoting pore formation, i.e. the 13-93 bioactive glass underwent reboil.

We hypothesised that the formation of open pores in SS316L originated from the closed pores, such that the closed pores merge into a larger pore in order to minimise their surface energy. When the large closed pore burst opened, a surface depression or a dent was left behind at the same location, forming an open pore, see inset of Figure 34a. However, the formation mechanism of open pores in LAM of 13-93 bioactive glass was different to that involved in an alloy. The viscous flow movement induced a shear stress that overcame the surface tension of the molten glass, broke open the closed pores and became open pores. From Figure 31 at 220 ms and Figure 34b, we observed that the open pores stopped growing after pore bursting.

In addition to pore formation, growth and bursting, we propose that Marangoni-driven flow facilitates pore migration during LAM. The Marangoni-driven flow entrains gas pores from the near surface and transports them near to the surface or the bottom of the melt track. During pore migration, pores coalesced and grew into larger pores; they were less likely to be released into the atmosphere, therefore, they resided near the melt track surface after solidification. We hypothesise that the growth rate of SS316L dendrites was much faster than the pore flow velocity, and thus the fast-growing dendrites trapped the gas pores at their grain boundaries. The viscous flow of 13-93 bioactive glass substantially dampened the Marangoni-driven flow, which restricted pore migration but facilitated pore coalescence and pore bursting in LAM. The viscous flow, reboil and vitrification of the 13-93 bioactive glass promoted pore
growth, and consequently it exhibited a significant amount of large pores, see Figure 33b and Figure 33c.

Unexpectedly, no spatter was evident during LAM of 13-93 bioactive glass. At the melting temperature of both samples, the viscosity of the molten 13-93 bioactive glass (2 Pa.S)\textsuperscript{243} was ca. 250 times higher than that of the molten SS316L (0.008 Pa.S)\textsuperscript{137}. The 13-93 bioactive glass had a much high resistance to the Marangoni-driven flow, and thus it prevented spatter formation. In contrast, the Marangoni-driven flow in SS316L combined with the argon gas expansion and metal vapour induced recoil pressure had led to ejection of low viscous liquid metal, forming droplet spatter. Our observations agreed with the spatter mechanism hypothesised by Khairallah \textit{et al.}\textsuperscript{38} who suggested that increased viscosity of the molten pool could possibly reduce spatter in LAM. Lastly, our results also demonstrate the first direct laser melting of 13-93 bioactive glass without a binder material.

3.5 Summary

A custom-built process replicator, LAMPR, has successfully integrated onto two high-speed synchrotron X-ray imaging beamlines to study the laser-matter interaction and powder consolidation of SS316L and 13-93 bioactive glass during LAM. Our key findings address the influence of powder properties to the laser absorption as well as the evolution of melt tracks and defects.

We conclude that the SS316L powder absorbs the laser energy at its surfaces, transferring the energy to the rest of the powder bed via heat conduction. The 13-93 bioactive glass absorbs the laser energy by the small traces of transition metal oxides in its composition. The melting of 13-93 bioactive glass is triggered by radiation conduction. The \textit{in situ} radiographs reveal that the melt tracks of SS316L and 13-93 bioactive glass are formed by molten pool wetting and viscous flow, respectively.

We demonstrate that LAM of a low viscous material (\textit{e.g.} SS316L) tends to form spatter during LAM owing to its low viscous resistance for retarding the fast Marangoni-driven flow. Conversely, LAM of a high viscous material (\textit{e.g.} 13-93 bioactive glass) prevents spatter formation during LAM by damping the Marangoni-driven flow. Beside spatter, the Marangoni-
driven flow promotes pore transport and gas release into the atmosphere during LAM, therefore the SS316L track only exhibits 0.03 % porosity. However, the viscous flow behaviour of 13-93 bioactive glass restricts pore transport, combined with the reboil effect, both facilitate pore coalescence and growth, forming large closed pores with a $D_{\text{avg}}$ of 529 µm, up to 10 times larger than those in SS316L. Therefore, the 13-93 bioactive glass track has resulted in a porosity of 17.6%.

We also reveal that the formation of open pores is due to pore bursting during LAM. Although the porosity is detrimental to the mechanical properties of the AM components, high degrees of porosity in 13-93 bioactive glass can potentially promote bone ingrowth when used for tissue engineering applications if the pore size distribution can be controlled.

We anticipate that LAMPR promises to become an innovative characterisation tool for advancing our understanding of the laser-matter interaction and powder consolidation and solidification in laser additive manufacturing.
Chapter 4 :

Shedding new light on laser additive manufacturing

Note a version of this chapter has been submitted to and under reviewed by Nature Communications: “Shedding new light on laser additive manufacturing”, Leung et al. 2017
Author contribution statement:

Chu Lun Alex Leung – Main investigator of this research who conceived the detailed idea, co-designed and built the experimental apparatus, submitted the beam time proposal, designed the experiments, performed experiments, data analysis, data interpretation and wrote up these results into this chapter.

Sebastian Marussi and Michael Towrie – Co-designed and built the experimental apparatus and provided comments on data interpretation.

Robert C. Atwood – Support in two separate beamline experiments and language corrections.

Philip J. Withers - contributed to the synchrotron proposal, provided comments on the data interpretation, results, and discussion.

Peter D. Lee – Conceived the overall project ideas, contributed to the synchrotron proposal and provided comments on the data interpretation, results, and discussion.
Abstract

The laser-matter interaction and solidification phenomena associated with laser additive manufacturing (LAM) remain unclear, slowing its process development and optimisation. Here, through in situ and operando high-speed synchrotron X-ray imaging, we reveal the underlying physical phenomena during the deposition of the first and second layer melt tracks. We show that the laser-induced gas/vapour jet promotes the formation of melt tracks and denuded zones via spattering (at velocities of 1 m s⁻¹). We also uncover new mechanisms of pore migration by Marangoni-driven flow (at velocities of 0.4 m s⁻¹), pore dissolution and dispersion by laser re-melting. We develop a mechanism map for predicting the evolution of melt features, including changes in melt track morphology from a continuous hemi-cylindrical track to disconnected beads with decreasing linear energy density; and improved molten pool wetting with increasing laser power. Our results clarify aspects of the physics behind LAM, which are critical for its development.
4.1 Introduction

Laser additive manufacturing (LAM), including laser powder bed fusion (LPBF) and direct energy deposition (DED), fuses metallic, ceramic or other powders to build up complex 3D shapes, layer by layer. LAM has attracted significant interest in academia and industry.\(^1\) The uptake of LAM in the production of safety-critical engineering structures, such as turbine blades, biomedical, and energy storage devices, is hindered by many technical challenges, including poor dimensional accuracy and entrainment of defects, e.g. lack of fusion, residual gas porosity, and spatter. All of these can act as stress raisers, leading to inconsistent mechanical performance of LAM components during service, posing a potential for catastrophic failure.\(^1\) To reduce defect formation in LAM a better understanding of the laser-matter interaction and powder consolidation mechanisms during LAM is required.

In LAM, the laser-matter interaction describes the reactions between a laser beam on powder particles, molten pool, or metal vapours. The powder consolidation involves the fusion of powder particles into a solid bead via laser melting. At present, the underlying mechanisms behind these processes are inadequately understood owing to the complex molten pool behaviour that occurs on very short time scales (10\(^{-6}\) - 10\(^{-3}\) s). Many key phenomena are partially revealed by real-time process monitoring devices within LAM machines, including spatter and line consolidation on the powder bed surface. These \textit{in situ} observations play a vital role in the development of computer simulations for LAM. However, the hydrodynamic behaviour inside the molten pool is insufficiently understood, hindering the development of process simulations tools for LAM.

High brightness third-generation synchrotron radiation sources enable X-ray radiography with unprecedented temporal (tenths of microseconds) and spatial (a few micrometres) resolution. This has been exploited to capture dynamic molten pool behaviour during laser welding, as well as the formation and evolution of keyhole pores and grain structure within single laser-induced molten pools. Here, we use \textit{in operando} synchrotron X-ray radiography along with a novel LAM process replicator (LAMPR) to image and quantify several new phenomena during the LAM of first layer and second layer tracks.
Here, we perform *in situ* and *operando* synchrotron X-ray imaging of LAM to investigate and quantify the defect and molten pool dynamics. We reveal and elucidate the mechanisms by which a melt track, denuded zone, spatter, and porosity form during LAM, including pore migration, dissolution, dispersion, and bursting. The presented methods and results can enhance the understanding of additive manufacturing and other materials processing technology, such as welding and cladding, in which porosity and spatter are common issues.

### 4.2 Methods

#### 4.2.1 Material characterization

The gas atomised Invar 36 powder (TLS Technik GmbH & Co. Spezialpulver KG) is selected for this experiment, because it is a material of interest for precision instruments, optical devices, electronic packaging, moulds and aircraft tooling owing to its low coefficient of thermal expansion.\footnote{–125} It was characterised by scanning electron microscopy (SEM) JEOL JSM-6610LV (Tokyo, Japan) and analysed using energy-dispersive spectroscopy (EDS). Example SEM images were shown in Figure 35a. We performed an elemental analysis using ANALYZER (Aztec, Oxford Instrument) in the same field of view. The elemental composition of the powder is shown in Figure 35b and Table 7. We segmented the particles using Otsu’s method\footnote{267} and then separated them by the watershed algorithm in the imaging toolbox of MATLAB 2016A (MathWorks, USA). Based on quantitative analysis of SEM images, we determined the particle size distribution was in the range of 5 - 70 µm with a \(d_{50}\) of 16 µm, see the labelled image in Figure 35c and the particle size distribution plot in Figure 35d.
Figure 35: Characterisation of Invar 36 powder: a, A backscatter scanning electron image of Invar 36 powder, b, an Energy-Dispersive X-ray (EDX) spectrum of (a) which indicates the presence of oxidised particles. c, powder particles from (a) are labelled with the area-equivalent diameter of individual particles. d, particle size distribution.

Table 7: Composition analysis of Invar 36 powder using SEM-EDS

<table>
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<tr>
<th>Element</th>
<th>Ni</th>
<th>Fe</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>O</th>
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<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>5.3</td>
</tr>
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</table>

4.3 In operando synchrotron X-ray radiography

To reveal the sequential thermophysical phenomena arising during LAM, we used the hard X-ray beamline I12: Joint Engineering Environmental and Processing (JEEP) at Diamond Light Source, UK for the operando synchrotron X-ray radiography experiments (Figure 36). The LAM process replicator (LAMPR) can be accommodated on the beamline and mimics an entry-level commercial LAM system. It comprises of a laser system, a loose powder bed with a packing density of 40 – 60%\(^{268}\) and an inert processing environment. The laser system consists of a 200 W ytterbium-doped fibre laser (wavelength of 1070 nm, TEM\(_{00}\), continuous-
wave (CW) mode, spot size of 50 µm, laser power ($P$) up to 200 W, and scan speed ($v$) up to 4 m/s, SPI Lasers Ltd, UK), an environmental chamber, IR reflective optics and a laser safety enclosure (Figure 36a). The laser beam was directed through a collimator, a beam expander, and an X-Y galvanometer scanner (Laser control systems Ltd., UK) coupled with an f-theta scan lens to focus its spot size down to 50 µm at the powder bed surface (Figure 36b). A full laser beam characteristic is shown in Appendix I.

A sample holder was positioned at the centre of the environmental chamber that securely held a powder bed of 30 mm x 3 mm x 0.3 mm (length x width x thickness) made out of a sandwiched structure of boron nitride (BN) plates (Figure 36c). In each experiment, loose powder particles of Invar 36 were loaded into the cavity of the powder bed by mechanical vibrations. Then, the sample holder was inserted into the environmental chamber via its side port. Once the environmental chamber was completely sealed, it was purged with argon gas at a flow rate of 4 l/min to reduce oxidation on the sample and metallic plume adsorption inside the chamber during LAM. Next, the laser beam scanned over a 4 mm line across the powder bed at 5 different scan speeds (9, 13, 17, 34 and 68 mm/s) and 3 laser powers (106, 157 and 209 W). The reported $P$ and $v$ values were calibrated after the in situ experiments (see details in Appendix I).

All experiments were performed using the LAMPR with a monochromatic X-ray beam at 55 keV and a high-speed X-ray imaging system, which comprised of a CMOS camera with a 12 GB high-speed internal memory (Miro 310M, Vision Research, USA) coupled with module 3 custom-made optics (I12: JEEP, DLS, UK). This provided a field of view (FOV) of 8.4 mm x 3.3 mm (width x height) and a pixel resolution of 6.6 µm. The image acquisition was synchronised with the LAMPR using a ring buffer mode that continued to record images into the internal memory of the camera until the laser was triggered. Before the laser trigger point, 100 images were recorded as flat field images, and then a further 100 dark field images were taken without switching on the X-ray beam. These two sets of images were taken for flat field correction to remove image artefacts caused by pixel variations and thermal counts during image acquisition. Once the laser was triggered, a series of radiographs were captured at 5100 fps (with an exposure time of 196 µs) using a 700 µm thick LuAg: Ce scintillator.
Figure 36: Experimental setup for the in situ laser additive manufacturing process replicator (LAMPR). a, LAMPR consists of an environmental chamber, a laser system, an IR reflector and a laser enclosure. The X-ray beam illuminates the environmental chamber via the X-ray window with the laser beam travelling from right to left (red arrow). b, A detailed schematic of the laser system demonstrating how the laser beam is collimated, expanded and focused before it reaches the powder bed; the laser beam can be steered in the horizontal plane by an X-Y galvanometer at various scan speeds. (c) Sectional views of the environmental chamber with an inset to demonstrate how the X-ray interacts with the metallic powder, which is held inside a cavity, sandwiched between X-ray translucent boron nitride (BN) plates.

4.4 Image processing and quantification

We processed all the acquired radiographs using MATLAB 2016a. Firstly, we applied a flat field correction using the following equation: FFC = (I_0 - Flatavg) / (Flatavg - Darkavg), where FFC is the flat field corrected image, I_0 is the raw image, Flatavg is the average of 100 flat field images and Darkavg is the average of 100 dark field images. These FCC images were denoised by VBM3D\textsuperscript{248}, followed by a custom background subtraction to remove most of the non-moving
objects. After that, the molten pool and droplet spatter were segmented using the Otsu’s method. The molten pool geometry (e.g. length, width, and area) were quantified by standard MATLAB built-in functions. The area shrinkage is calculated by (maximum molten pool area at the onset of the cooling stage – molten pool area after cooling) / (maximum pool area) x 100 %. Furthermore, we used the Manual Tracking plugin from ImageJ to track the movement of the droplet spatter and pores in the first layer (MT1) and second layer melt track (MT2). The distance and average velocity were computed based on the pixel locations obtained from individual trajectory path and duration of each event. A detailed image processing flow chart and the resultant processed images are shown in Appendix Figure 2 and Appendix Figure 3, respectively.

4.5 Results and discussion

In this study, we examine the fusion of powder particles on top of a loose powder instead of on a solid substrate; which is a geometry we refer to as the ‘overhang condition’ and is often encountered when building up complex 3D shapes. The scan speed was selected to enable a continuous track to be formed.

4.5.1 Evolution of a single layer melt track during LAM

We captured the evolution of a single layer melt track (MT1) during LAM by in operando high-speed synchrotron X-ray radiography (Figure 37). Based on the greyscale images, we can see that the Invar 36 powder (light grey) attenuates less X-rays compared to that of the molten pool or a melt track (dark grey). This is because the effective density of the powder is only 40 – 60 % that of a molten pool or a melt track. Figure 37a shows the changes in melt track morphology at the onset, middle, and final stages of LAM. At time, t = 0, the laser beam (P = 209W and v = 13 mm/s) switches on. It scans leftwards across the powder bed and consolidates powder particles into a molten pool (t = 2.8 ms), and subsequently evolves into a melt track which extends towards the bottom of the powder bed (t = 338 ms). As the melt track cools, it bends upward, followed by pore formation in the last solidified region of the melt track (t = 400 ms). The four red dotted boxes and their magnified views highlight the evolution of powder consolidation (Figure 37b-d), spatter (Figure 37e) and porosity (Figure 37f) during LAM.
During the initial stages of LAM (Figure 37b), a molten pool forms ca. 100 µm (ca. twice the size of the laser spot size) below the powder bed surface (t = 1.8 ms) and rapidly grows into a 250 µm sphere (t = 2.8 ms). Its growth rate slows as it reaches an equivalent diameter of 400 µm (Figure 37c), because powder spatter removes a significant amount of powder particles ahead of the laser beam, leaving a powder-free zone (or denuded zone) normal to the melt surface, so that there are fewer powder particles available for subsequent powder consolidation. Consequently, the laser beam moves ahead and forms a new molten pool further along the scan path (t = 7.2 ms). The growth rate of this newly formed molten pool is faster than v, thus the laser beam heats the molten pool whilst lowering its surface tension which promotes wetting. Consequently, the newly formed molten pool coalesces with the first melt bead via wetting (t = 7.4 ms), revealing a key track growth mechanism (see Figure 37c). The combination of Marangoni convection inside the molten pool and the inward gas flow above the molten pool causes the molten pool to oscillate throughout LAM.

The intense laser beam (power density of ~10^6 W/cm^2) causes metal vaporisation at the molten pool surface and generates a recoil pressure in the laser-matter interaction zone, resulting in a gas/vapour jet. We hypothesise that the metal vapours heat the argon gas causing rapid gas expansion, resulting in a vapour jet that expands radially at high-speed. This laser induced gas/vapour jet entrains powder particles into a melt track which is a key track growth mechanism (Figure 37d). It also induces powder spatter from the laser-matter interaction zone (Figure 37e) while forming a denuded zone. Unlike the droplet spatter mechanisms reported previously in which the spatter ejects from the melt track, here the majority of the droplet spatter during LAM in the overhang configuration originates from molten pools ahead of the melt track or melting of powder spatter by the laser (Figure 38a).

Hot ejection has a diameter greater than 40 µm (or ~6 pixels) and it appears as black in the X-ray images as compared to cold powder agglomerates (which are less dense than the hot ejection and hence a dark grey colour in the X-ray images). Our results reveal that, in addition to the individual particle ejection, cold powder agglomerates are also ejected, interacting with the laser beam to become molten, transforming cold ejection into hot spatter. Although neither studies have a direct temperature measurement, our results support and build on the hypothesis of Ly et al. on the formation of cold and hot ejections during LAM.
The droplet spatter ejects vertically ($t = 170$ ms in Figure 37e) and it follows the flow direction of the argon gas ($t = 180$ ms in Figure 37e). We also reveal, a less common phenomenon, laser induced gas expansion in a droplet spatter (Figure 38b). Our observations on spatter formation under the overhang configuration complement those of Ly et al.\textsuperscript{209} on spatter formation during deposition on a solid substrate. These images also explain why it is very difficult to produce a horizontal overhang feature because the melt track always extends towards the bottom of the powder bed as a result from spatter formation. Future work is needed to mitigate this track extension issue.

It is evident that the volume of material added to the melt track by molten pool wetting exceeds the amount of material added by the vapour-driven powder entrainment, suggesting molten pool wetting is the primary track growth mechanism. The melt track continues to grow until the laser switches off at 334 ms. At this time, no porosity is evident in the melt track and spattering has also stopped (Figure 37f). As the melt track cools, the gas solubility reduces significantly in the liquid metal\textsuperscript{270,271}, forming gas pores (e.g. hydrogen\textsuperscript{272} or nitrogen\textsuperscript{273,274}) ahead of the solid/liquid interface ($t = 384$ ms). These gas pores possibly originated from the residual porosity in the powder\textsuperscript{156}, residual moisture on the powder surface, or inside the environmental chamber, which can easily transfer into the molten pool during LAM. Our results show that the majority of pores are swept outward and downward along the solidification front by Marangoni flow, before rising in the middle of the pool and recirculating with velocities up to 0.4 m/s (see quantification later). As solidification progresses the melt flow velocity reduces and buoyancy forces exerted by the pores dominate, causing the pores to reside near the track surface with some pores coalescing to form larger pores ($t = 390$ ms). Towards the end of the solidification, a few pores adjacent to the top surface escape into the atmosphere via pore bursting, leaving a depression at the melt track surface (orange dotted circle, $t = 406$ ms). These features are identical to the open pores observed by Qiu et al.\textsuperscript{144}. They hypothesised that the formation of open pores was due to incomplete melting or insufficient liquid feeding, however, we reveal that they were formed by pore bursting.
Figure 37: Time-series radiographs acquired during LAM of an Invar 36 single layer melt track (MT1) under $P = 209 \text{ W, } v = 13 \text{ mm/s and } E_l = 16.1 \text{ J}$. a, The melt track morphology at three key stages of LAM. b, The formation of a molten pool and a denuded zone (yellow dotted line). The laser beam causes the molten pool to vaporise, generating a recoil pressure at the interaction zone (blue dotted arrows) whilst indirectly heating up the surrounding argon gas (red arrows). The molten pool/track grows while enlarging the denuded zone by: c, wetting and d, vapour-driven powder entrainment (blue dotted circle) which can lead to the formation of e, powder spatter (blue dotted circle) and droplet spatter (green arrows). After the laser switches off at $t = 334 \text{ ms, f, pores nucleate, coalesce and burst, resulting in an open pore (orange dotted line). All scale bars, 250 } \mu\text{m}$. 
Figure 38: Additional spatter mechanisms: a, the formation of droplet spatter by laser melting of powder spatter (see blue dotted circle) and b, laser induced gas expansion in a droplet spatter (see green dotted circle).

4.5.2 Influence of process parameters on melt track evolution

To gain a better understanding of LAM, we conducted a systematic set of 15 trial runs to investigate the effects of laser power \( (P) \), scan speed \( (v) \), or linear energy density \( (LED = P/v)^{112,276} \) on the evolution of the molten pool dynamics (see Figure 39). Each trial uses a laser power density (\( \sim 10^6 \, \text{W/cm}^2 \)) sufficient to form molten pools. In order to visualise the progress of melt features over time, for each \( LED \) condition, the resulting series of radiographs are transformed into a single time-integrated image by overlaying the time coloured segmented tracks on top of each other in reverse chronological order (Figure 39a). We form a mechanism map by combining these time-integrated images with respect to their process parameters (Figure 39b). Unlike the traditional \( P-v \) process map\(^{133} \) which shows only the final melt track morphology obtained from post-mortem analysis,\(^{276} \) Figure 39b shows the dynamic changes occurring in the molten pool and also reveals the underlying phenomena associated with 15 different combinations of \( P \) and \( v \).

At constant \( P \), the morphology of the melt track undergoes two transitions as \( v \) increases: firstly from continuous hemi-cylindrical track to two or more discontinuous hemi-cylindrical tracks, and secondly from discontinuous hemi-cylindrical tracks to a series of separated molten beads, i.e. balling\(^{111} \).
Increasing \( v \) reduces the laser energy transferred to the powder particles, thereby reducing the molten pool size and its peak temperature. When the molten pool temperature is low, its surface tension increases, reducing the driving force and time for it to coalesce onto the pre-existing melt features, forming discontinuous tracks. Upon increasing \( v \) further (i.e. reducing LED to < 4 J/mm), the laser beam now moves faster than the growth rate of the molten pool so that the liquid metal immediately curls up into a sphere to minimise its surface energy. Spheroidisation of metal beads repeats itself until the laser beam switches off, resulting in balling. In overhang configuration the proposed balling mechanism is mainly due to the reduction of surface tension, contrary to the balling mechanism induced by the Plateau-Rayleigh instability during LAM on a solid substrate.\textsuperscript{113}

Increasing \( P \) delivers more laser energy for powder consolidation while improving molten pool wetting; reducing \( v \) increases the laser-matter interaction time. Both effects increase the likelihood of forming a continuous hemi-cylindrical track by increasing the molten pool temperature which reduces its surface tension and promotes molten pool wetting. In contrast, the movement of the liquid metal becomes less violent with increasing \( v \) and decreasing \( P \) (i.e. decreasing LED).

Furthermore, Figure 39b shows that melt tracks exhibit similar morphology when processing at constant LED (e.g. 3.1 J/mm). For overhang configurations, the minimum LED required to form a continuous Invar 36 melt track is ca. 16 J/mm whereas the minimum LED to make Invar 36 parts on a solid substrate only requires a LED of 0.2 J/mm\textsuperscript{125}. The large difference in LED, because the effective thermal conductivity of the powder bed (present study) is lower than that of building on a solid starting block.\textsuperscript{277} In addition, the wettability of the molten pool is significantly lower when building on powder support than building on a solid starting block or a prior solid track.\textsuperscript{126} For both reasons, a slower \( v \) is required to form a continuous track on powder support as compared to solid; therefore, we have used different processing conditions to those used by Qiu et al.\textsuperscript{125}. The mechanism map (Figure 39b) reveals morphological transitions of the melt track similar to reference studies\textsuperscript{113,125,126}, suggesting that the processing regime we selected is reasonable for laser melting directly on powder support.
Figure 39: Time-resolved melt track morphologies under different process parameters. a, Steps to produce a time-integrated image. Each time-series of radiographs is segmented and labelled with time, and then flattened into a time-integrated image. b, A mechanism map combines 15 time-integrated images, showing the dynamic changes of molten pool behaviour and melt track morphologies with respect to $P$, $v$ and $E_L$ (indicated by the numeric value at the corner of each time-integrated image). Red arrows indicate the scan direction of the laser beam. The black dotted line indicates the powder bed surface. Scale bars, 2 mm.

We have selected three continuous tracks (highlighted by the orange outline in Figure 39b) and quantified the changes in the melt track geometry over time. The track lengths are found to be $19.3 \pm 0.3\%$ longer than the nominal scanned length (4 mm). The quantification results show that these melt tracks have undergone $3 - 5\%$ solidification shrinkage (see Figure 40a and Table 8). Compare to an industrial AM process, Ning et al.\textsuperscript{278} reported that the part
shrinkage ranges from 0.8 % to 9.8 % based on a track length from 3 to 70 mm, respectively. They showed that for a track length of 6 mm, the AM part underwent a shrinkage of 5.2 % which matched very well with our quantified shrinkage results. These real-time measurements of the molten pool geometry can be used for verifying existing model simulation tools for the prediction of build accuracy in LAM.

Figure 40: Time-resolved quantification of three continuous melt tracks by image analysis: a, the length (red), width (blue) and b, the overall area shrinkage of the molten pool (%) (black). The inset illustrates the melt track after the laser switches off (334ms), overlaid with outlines of the melt track at 334 ms (red) and 998 ms (blue). Scale bar, 500 μm.

Table 8: Result summary from Figure 40

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<th>v (mm/s)</th>
<th>LED (J/mm)</th>
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4.5.3 Melt track evolution during layer wise LAM

While much can be learned from observing the laser-matter interaction in the overhang configuration, it is a common practice in LAM to build a part by adding a melt track on top of another track. Hence, we add a second powder layer on MT1 and perform another trial under
identical process conditions to MT1 to form a second layer melt track (MT2). Our results reveal the thermophysical interactions between MT1 and MT2 during LAM (Figure 41a-d) and three new pore formation mechanisms (Figure 41i-k).

The initial powder consolidation phenomena in MT2 (< 5 ms) are similar to those observed in MT1, in which the laser creates a small denuded zone while forming a molten pool just below the powder level (Figure 41a). The molten pool grows until it reaches a diameter of ca. 300 µm, over half the diameter of that in MT1 (ca. 500 µm). Then the molten pool wets onto the surface of MT1 (Figure 41e), causing it to undergo re-melting. This can be seen by the greyscale (and density) changes when the solid changes into a liquid and back. The mechanism by which a second (or nth) layer forms shows how the underlying layer facilitates track growth via molten pool wetting. This explains why it is much easier to form a melt track on a solid substrate than in the overhang configuration.

In addition to track growth, molten pool wetting also plays a key role in pore formation and growth (see Figure 41e-h). Marangoni-driven melt flow causes the liquid metal (with a high surface tension) to fold over the surface of MT1 (Figure 41f), entraining an argon bubble\cite{38,279} (yellow dotted circle in Figure 41g). Since the argon gas solubility is < 0.1 part per billion in the Fe-based alloy\cite{280,281}, argon is expected to release into the atmosphere. The Marangoni-driven flow also entrains a thin powder layer between MT1 and MT2 indicated by the abrupt changes in the image contrast at the centre of the red dotted circle in Figure 41h. If the thin powder layer remains in between the melt tracks, this could lead to the formation of lack of fusion defects and interlayer pores.

In contrast to the MT1 trials, porosity nucleates and grows throughout LAM of MT2 rather than only after the laser switches off. We hypothesise that MT1 acts as a heat sink, conducting a significant amount of heat energy from the laser-matter interaction zone, causing a rapid solidification of MT2 and promoting the formation of gas pores. The large temperature gradients in MT2 cause large variations in surface energies and concomitant Marangoni forces, resulting in a fast melt flow, swirling the pores inside the melt track and along the scan direction of the laser beam. This removes many interlayer pores by allowing them to flow towards the surface and escape from the melt track.
In addition to the new pore growth mechanism, we also see pore dissolution and dispersion mechanisms involved during LAM of MT2 (Figure 41c, i-k). At the end of MT2, many of the powder particles above MT1 are removed via spattering (purple dotted circle Figure 41d); hence the laser beam re-melts a large portion of MT1 (see the re-melting zone (RZ) in Figure 41d). Laser re-melting promotes existing pores in MT1 to coalesce and grow at the expense of others (Figure 41i), reducing the pore density. These gas pores possibly originated from residual air from the chamber, the gas porosity in the powder or from moisture on the powder surface (or inside the environmental chamber), which can easily transfer into the molten pool during LAM through entrapment of nitrogen from residual air or dissociation of moisture into hydroxide and soluble hydrogen, respectively. The solubility of nitrogen and hydrogen increases with temperature, and hence gas pores would dissolve back into the melt (Figure 41j). After the laser switches off, small pores reappear in MT2 during cooling (Figure 41k); suggesting laser re-melting disperses large pores into smaller ones rather than eliminate them.

In the MT2 experiment, we have observed that droplet spatter fails to eject completely, it grows via powder amalgamation while rolling along the top surface of the BN walls (purple dotted circle, Figure 41c). This phenomenon is unlikely to carry forward to a commercial AM process, because the droplet spatter is expected to be redeposited onto a melt track. Due to the thin powder bed, the melt track is in contact with the BN walls, restricting the hot argon gas flow inside the powder bed, resulting in powder spatter at both sides of the melt track (Figure 41c-d). The BN walls accentuate the side ejection of powder, further supporting the hypothesis that argon gas expansion contributes to spatter formation.
Figure 41: Time-series radiographs acquired during LAM of an Invar 36 second layer melt track (MT2) under $P = 209$ W, $v = 13$ mm/s and $E_L = 16.1$ J/mm. Snapshots of MT2 at various stages of LAM: a, Formation of a molten pool on the second powder layer. b, Growth of MT2 via wetting on MT1. c, MT2 undergoes laser-re-melting, where RZ indicates the laser re-melting zone. d, MT2 completely solidifies. (c-d) The large droplet spatter (purple dotted circle) failed to eject from the powder bed. Other key phenomena involved during molten pool wetting: e, Re-melting of MT1. f, Extension of MT2 before wetting on MT1. g, Entrapment of gas bubble (see yellow dotted circles) and h, thin powder layer (see red dotted circles). Three new pore evolution mechanisms induced by laser re-melting: i, pore coalescence, j, dissolution, and k, dispersion. Scale bars, 500 µm.
4.5.4 Time-resolved quantification of droplet spatter and pores

To reveal the underlying defect formation and growth mechanisms, as well as the hydrodynamic behaviour of the melt fluid, we track the movements of droplet spatter and pores during the evolution of MT1 and MT2. We overlay a typical spatter trajectory path on a radiograph (Figure 42a) to illustrate how the spatter is tracked. Due to the spatial resolution of the radiographs, we are only able to track spatter having a size range of 40 – 350 µm. The size range is lower than what has been reported by Andani et al.282,283 who quantified spatter particle having a diameter in the range of 150 - 750 µm in an industrial machine, SLM 280HL (SLM solutions Inc. Germany).

The spatter trajectories predominately eject towards the gas flow or the laser scanning direction (Figure 42b). During the formation of MT1, droplet spatter usually originates near the denuded zone (Figure 42b). The laser heats a large powder volume with a large surface area, inducing metal vaporisation while indirectly heating the argon, creating a strong jet that causes powder and droplet spatter to move at high velocities (Figure 42c). During the formation of MT2, the laser beam fuses the powder layer with MT1 so that much of the heat energy is transferred to MT1, and hence only small amount of energy contributes to gas/vapour jet and spatter formation. Unexpectedly, the majority of droplet spatter in MT2 forms as the powder spatter passes through the laser beam approximately 300 µm above the powder bed surface. This shows droplet spatter is more likely to form under an overhang configuration than LAM on a solid substrate (Figure 42c). This confirms that the hot argon gas assists the formation of droplet spatter.

The flow directions and velocities of liquid metal can be determined by tracking the pore motion. A tracked pore trajectory verifies the expected dominance of centrifugal Marangoni convection (Figure 42d).141 The melt zone in MT2 is much smaller than that in MT1 (Figure 42d), because most of the heat energy conducts towards MT1, resulting in a high thermal gradient at the melt zone of MT2. We hypothesise that the liquid metal flows three times faster in MT2 than MT1, this is supported by the mode pore velocity of MT2 is 75 mm/s compared to that of 25 mm/s in MT1 (Figure 42e).
Figure 42: Tracking the movement of pores and spatters during LAM of MT1 and MT2. a, An example of a spatter trajectory overlays on a radiograph. b, An overlay image contains all the spatter trajectories. c, A histogram of the average spatter velocities. d, An example of a pore flow trajectory overlays on a radiograph. The centrifugal Marangoni-driven flow forces the pore to flow in a clockwise direction. e, A histogram of the average pore flow velocities.

4.6 Summary

In summary, we have used synchrotron X-ray imaging to uncover key mechanisms of laser-matter interaction and powder consolidation in situ and operando during LAM, including the formation and evolution of the melt tracks, porosity, spatter, and denuded zone. Further, the time-resolved quantification of the pore and spatter movements give crucial information of their velocities and direction, not possible to acquire using other techniques. We have demonstrated that Marangoni convection dominates the liquid metal flow, reaching a velocity of 400 mm s⁻¹. Our mechanism map provides new insight into the dynamic changes in melt track behaviour.
across a range of process parameters, *e.g.* improved molten pool wetting with increasing $P$, and the morphological transition from first a continuous to an interrupted hemi-cylindrical melt track and a series of independent molten beads as $v$ increases. The methodology introduced here also sheds new light on the mechanisms of pore formation, including the migration, dissolution, dispersion, and bursting of pores during LAM. Future investigations in these areas will deepen our fundamental understanding of the nature of the laser-matter interaction.
Chapter 5:
Defect mechanisms in laser powder bed additive manufacturing revealed by synchrotron X-ray imaging

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Author contribution statement:

Chu Lun Alex Leung – Main investigator of this research who conceived the detailed idea, co-designed and built the experimental apparatus, submitted the beam time proposal, designed the experiments, performed experiments, data analysis, data interpretation and wrote up these results into this chapter.

Sebastian Marussi and Michael Towrie – Co-designed and built the experimental apparatus and provided comments on data interpretation.

Robert C. Atwood – Support in two separate beamline experiments and language corrections.

Philip J. Withers - provided comments on the data interpretation, results, and discussion.

Peter D. Lee – provided comments on the data interpretation, results, and discussion.

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Abstract

Understanding defect formation mechanisms during laser-matter interaction and powder consolidation are key to optimise the properties of additive manufactured components. In this study, we elucidate the phenomena by which porosity and spatter evolve during laser additive manufacturing (LAM) of virgin and oxidised Invar 36 powders under overhang and layer wise build conditions using \textit{in operando} synchrotron X-ray imaging. During LAM, oxides from the powder are found to concentrate in the molten pool, altering the direction of the Marangoni convection from an inward to an outward flow. This sweeps the gas pores to the bottom of the molten pool, restricting gas escape from the melt track and promoting porosity. We uncover that pore bursting can result in two different outcomes: (1) inducing a Marangoni flow to heal pores or (2) forming droplet spatter and open pores. The laser-induced vapour jet at the melt surface forms a material free zone by forming spatter. Our results show that spatter occurs more frequently when LAM takes place under an overhang condition than a layer wise condition. Notably, we demonstrate that droplet spatter can be formed by indirect laser-driven gas expansion instead of forming spatter by the laser-induced metal vapour at the melt surface. We also show that laser re-melting reduces the size and number density of pores by promoting gas release via the keyhole or partially filling the pore via liquid feeding.
5.1 Introduction

Laser additive manufacturing (LAM) selectively fuses powder particles together using a focused laser beam (with a peak power density of > 10^6 W cm^2), layer-by-layer, to build up complex 3D objects.\textsuperscript{261} It offers great promise in aerospace, nuclear fusion, and energy storage applications.\textsuperscript{13} However, the uptake of LAM in these areas is mainly hindered by inconsistent part performance, \textit{e.g.} mechanical\textsuperscript{22,51}, thermal and electrical properties\textsuperscript{15}, owing to the presence of defects \textit{e.g.} pores and spatter in the additive manufactured components.\textsuperscript{11,58}

The defect formation mechanisms are difficult to characterise owing to the fast laser-matter interaction (10^{-6} - 10^{-3} s).\textsuperscript{108} Although model simulations could be used to reveal some of the missing physics in additive manufacturing (AM) processes\textsuperscript{38,40}, they demand experimental data for model validation and verification, such as real-time data regarding the molten pool dynamics. This data can be collected using \textit{in situ} monitoring devices installed on AM systems.\textsuperscript{42,43} However, these devices are unable to reveal the dynamic behaviour of the melt features \textit{e.g.} porosity and spatter or the interactions between two or more melt tracks over time. \textit{In situ} X-ray radiography has been used to capture the underlying mechanisms of solidification phenomena\textsuperscript{237,238} and dynamic molten pool behaviour during laser welding\textsuperscript{222,225}. Recently, Zhao \textit{et al.}\textsuperscript{227} studied the molten pool dynamics and phase transformation inside a molten pool during laser powder bed fusion (LBPF) using synchrotron X-ray imaging combined with X-ray diffraction. However, the molten pool dynamics inside the melt track or interactions between two or more melt tracks during LAM remains unclear.

Many different mechanisms for the formation of closed pores in AM have been hypothesised, including powder contaminations\textsuperscript{154}, coating defects\textsuperscript{285,286}, the presence of carbon\textsuperscript{142}, hydrogen\textsuperscript{118,287} and oxide inclusion\textsuperscript{55} in the molten pool, internal gas porosity\textsuperscript{118,130,142,144,156,287,288}, keyhole collapse\textsuperscript{145} and entrapped gas during melting\textsuperscript{195}. Experiments demonstrating when each of these mechanisms is active and how porosity evolves, especially for irregular\textsuperscript{55,142,289} and open pores\textsuperscript{144}, are required.

Besides porosity, powder spatter\textsuperscript{51,208,209} and droplet spatter\textsuperscript{51,290} are two common defect found in LAM. They influences the resultant porosity\textsuperscript{22,144,291} and surface finish\textsuperscript{22} of AM
parts. Several studies reported that spatter causes powder bed contamination, improper powder spreading and damages the equipment inside the AM system.\textsuperscript{51,253,284,292}

Powder spatter\textsuperscript{51} or denudation of powder\textsuperscript{208} is induced by the interactions between metal vapour and Bernoulli effect-driven gas flow, \textit{i.e.} metal vapour-driven particle entrainment.\textsuperscript{208,209} Bidare and Bitharas \textit{et al.}\textsuperscript{210} correlated the evolution of spatter to the direction of the metallic plume generated from LAM.

The formation of droplet spatter is very complex and its initiation mechanism is still not well understood. The formation of spatter may also begin with a molten pool instability due to local boiling or melt evaporation\textsuperscript{38,124,144}, accumulation of recoil pressure\textsuperscript{51,209,293}, combining with melt flow acceleration by Marangoni convection, resulting in a stream of liquid ejecting in a vertical direction.\textsuperscript{38,51,208,220,293,294}

Therefore, understanding these underlying mechanisms behind the formation of porosity and spatter are key enablers to predict and control the properties of LAM components. In this paper, we use a combination of a laser additive manufacturing process replicator (LAMPR) and \textit{in operando} high-speed synchrotron X-ray imaging to elucidate several new mechanisms regarding the formation of porosity and spatter during LAM of multi-layer Invar 36 samples. We also investigate the effects of oxide on the molten pool dynamics. In order to support our analysis, we have quantified the molten pool geometry, solidification shrinkage and porosity (%) over time, in addition, using \textit{a posteriori} X-ray computed tomography (XCT) to visualise and quantify the porosity in 3D.

5.2 Experimental methods

5.2.1 Powder characterisation

The morphology and chemical composition of a gas atomised Invar 36 powder were characterised by a JEOL JSM-6610LV scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). The powder particle distribution was extracted using SEM images and Image Processing Toolbox in MATLAB 2016a (The Mathworks Inc, USA). X-ray Diffraction (XRD) was performed on the Invar 36 powder using a PANalytical X’Pert Pro MPD series automated spectrometer (Malvern Instruments, UK), CuK\textsubscript{α} radiation (λ =1.541Å)
at 40kV and 40mA, a 2θ scanning range (degrees) was 10° to 100° with a step size of 0.03°, and a count rate of 50 s per step. After XRD, we performed phase identification in Profex.²⁹⁵

5.2.2 Real-time and in operando LAM with synchrotron X-ray imaging

To reveal the effects of the presence of oxide on the fluid dynamic behaviour during LAM of Invar 36, we used the LAMPR to perform two separate AM builds, one year apart from each other, under overhang conditions. The overhang conditions described that powder particles were directly fused together above loose powder instead of fused together on a solid substrate. In each build, the LAM process was monitored by high-speed synchrotron X-ray radiography in the Beamline I12: Joint Engineering Environment Processing (JEEP) at Diamond Light Source.²⁶⁹

A laser beam (wavelength of 1030 - 1070 nm, transverse mode TEM00, continuous-wave (CW)) scanned a 4 mm line at a power of 150 W and a nominal scan speed of 5 mm/s across the Invar 36 powder bed (30 mm length, 0.3 mm wide and 3 mm deep) in an argon atmosphere at a flow rate of 4 l/min. For the first AM build (B1), we performed LAM of a single layer track using an Invar 36 virgin powder. After that, the virgin powder was kept in a container and exposed to air for a year to permit particles to undergo oxidation. For the second AM build (B2), we produced a single layer track from the oxidised Invar 36 powder using the same experimental conditions as B1. After that, we built two additional melt tracks above the first melt track in B2 while performing X-ray imaging experiment. This provided new evidence to elucidate the molten pool dynamics and defect mechanisms during LAM.

The current version of LAMPR was not equipped with a movable platform to lower the melt track after each experiment or an auto-powder layering module. The powder deposition was performed manually, and hence the layer thickness varied depending on how the prior melt track was formed. A slow scan speed was chosen to ensure continuous tracks can be formed under overhang configurations.

All experiments were captured at 5100 frames per second (fps) using 55 keV monochromatic X-rays, custom module optics with a 700 µm thick LuAg: Ce scintillator coupled with a Miro 310M camera (Vision Research, USA). Using a region of interest mode, the field of view (FOV) of the camera was 8.4 mm in width and 3.3 mm in height with a 6.6 µm
pixel size. The image acquisition system was synchronised with the LAMPR using a ring buffer mode that continuously recorded images into the on-board memory of the camera. In each experiment, we captured one hundred dark-field images (with the X-ray beam off) and one hundred flat-field images (with the X-ray beam on but without the sample). Once the laser was triggered, twelve thousand radiographs were recorded onto a local hard drive.

5.2.3 *Posteriori* XCT and metallography

After the *in operando* radiography experiments, both melt tracks were further examined by a *Nikon* XTH 225 X-ray microfocus tomography system (*Nikon*, Japan), see acquisition parameters in Table 9. The radiographic projections from each XCT scan were reconstructed into a 16-bit 3D image volume using built-in beam hardening correction and filtered back projection algorithms in CT Pro3D (*Nikon*, Japan).

**Table 9:** XCT acquisition parameters for the imaging of Invar 36 melt tracks

<table>
<thead>
<tr>
<th>Sample - build number</th>
<th>Accelerating voltage (kV)</th>
<th>Beam current (µA)</th>
<th>Number of projections</th>
<th>Exposure time (ms)</th>
<th>Scan volume (mm³)</th>
<th>Voxel size (µm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>100</td>
<td>100</td>
<td>1200</td>
<td>500</td>
<td>7.2³</td>
<td>3.6</td>
</tr>
<tr>
<td>B2</td>
<td>100</td>
<td>100</td>
<td>3142</td>
<td>500</td>
<td>4.8³</td>
<td>2.4</td>
</tr>
</tbody>
</table>

5.2.4 Image processing and quantification

These acquired radiographs were post processed and analysed using MATLAB 2016A. They were normalized by flat field correction\(^{296}\) to remove image artefacts. A denoise algorithm, VBM3D\(^{248}\), was then applied on these normalised images, followed by a custom background subtraction and segmentation. We extracted and quantified the melt track geometry (*e.g.* length, depth and area), porosity and area shrinkage.
5.3 Results and discussion

A particle size distribution of Invar 36 is in the range of 5 – 45 µm with a mode of 10 µm (Figure 43). The inset SEM image overlaid with an EDS oxygen map shows that the Invar 36 powder particles for B2 are mostly spherical and their surfaces are covered with oxides (Figure 43a). The EDS results show the chemical composition of Invar 36 consists of $67.2 \pm 0.2$ wt. % Fe, $30.4 \pm 0.2$ wt. % Ni and $2.3 \pm 0.1$ wt.% O. The XRD pattern only shows the presence $\gamma$-(Fe, Ni) phase (face centre cubic) in Invar 36 powder (Figure 43b). However, the phase diagram of Invar 36 shows that the $\alpha$-(Fe, Ni) phase can also be formed at low temperature$^{297}$ but it has not been detected by the XRD instrument. Qiu et al.$^{125}$ suggested that the volume fraction of $\alpha$-(Fe, Ni) is below the detection limit of laboratory XRD instruments.

![Invar 36 Particle Size Distribution](image)

**Figure 43**: Powder characterisation of Invar 36: **a**, Particle size distribution. The inset shows an EDS map of oxygen overlaid on a SEM image of Invar 36 powder. **b**, XRD pattern of Invar 36 showing the presence of $\gamma$-phase.

### 5.3.1 LAM of virgin and oxidised Invar 36 powder

Figure 44a displays the onset, middle and final stages of the melt track during LAM in B1. The high power density ($\sim 10^6$ W/cm$^2$) laser beam fuses the Invar 36 particles to form a molten pool, and subsequently vaporises the molten pool to form a metal vapour jet.$^{208,209}$ We hypothesise that the metal vapour jet indirectly heats the gas particles in the laser-matter interaction zone via phonon vibrations between the plasma and the gas particles. The
combination of metal vapour jet and hot argon gas causes an entrainment of powder particles into the molten pool and promotes track growth. When the laser beam moves faster than the growth rate of the molten pool, it produces a molten pool ahead of the main melt track. The Marangoni-driven flow causes the newly formed molten pool to move in the opposite of the laser scanning direction and merge with the melt track. The aforementioned track formation mechanisms are summarised as molten pool wetting and vapour-driven powder entrainment. No pores are evident as the melt track extends but powder and droplet spatter ejects frequently from the powder bed towards the direction of the laser beam and argon gas flow, similar to what has been reported by Anwar et al.284.

**Figure 44b** shows the evolution of a first layer melt track (L1) in B2. L1 is formed by the similar track formation mechanisms depicted in B1. Clearly, L1 exhibits a high degree of porosity in B1 compared to B2. The time-series radiographs demonstrate that a droplet spatter positioned on the left-hand side of the laser beam (**Figure 44a**) rotates in a clockwise direction whereas pores (**Figure 44c**) located on the right-hand side of the laser beam flows in an anti-clockwise direction. They indicate that the melt flows radially outwards and follows the centripetal Marangoni convection. In contrast to our observations, most molten metals or alloys, including Fe-Ni alloys298,299, should flow radially inwards owing to their negative temperature coefficient of surface tension, *i.e.* follow the centrifugal Marangoni convection. Well-established theories in solidification and laser welding suggest that the presence of oxygen in the molten pool (ca. 50 ppm) is sufficient to alter the temperature coefficient of surface tension from negative to positive, changing the Marangoni convection from an inward to an outward flow138,141, see **Figure 45**.

**Figure 44c** and **Figure 44d** show two types of pores can be formed during LAM. Type I pores are identified as gas pores with a diameter less than 250 μm, a low solubility and high buoyancy in the melt, see examples in **Figure 44c**. They usually form near the laser beam and reside near the melt track surface due to its high mobility. During LAM, the Marangoni-driven flow entrains the type I pores to different locations inside the melt track. Meanwhile, some pores coalesce to form larger pores and some escape into the atmosphere via a keyhole or by pore bursting. In terms of the gas escape mechanism via the keyhole, Huang et al.300
hypothesised that gas bubbles could break through the thin keyhole wall and escaped during electron beam welding.

Type II pores are identified as pores that are covered with an oxide layer. Their sizes vary from a few tens to over hundreds of microns. They usually locate a few hundred microns away from the laser beam and melt track surface. They remain stationary throughout LAM, except for during pore growth. Our results reveal that the large type II pores grow at the expense of type I pores via Ostwald ripening and hence the diameter of type II pores is at least 250 μm, see examples in Figure 44d.

**Figure 44:** Times-series radiographs showing melt features observed during LAM of a first layer Invar 36 melt track (L1) with a power of 150 W and a scan speed of 5 mm/s. Overviews of a continuous track produced from a, virgin powder and b, oxidised powder, showing key features of track formation, spatter and porosity. The region of interest (ROIs) show two distinctive pore evolution mechanisms: c, Pore coalesce and migration by the centripetal Marangoni convection and d, pore growth promoted by oxide films, see examples highlighted by orange and yellow circles.
Figure 45: Schematics of Marangoni convection during LAM of a, virgin powder and b, an oxidised powder. (a) Liquid metal with a negative temperature coefficient of surface tension shows gas entrainment and (b) the oxide films alter the flow direction, restrict the melt flow area and promote pore growth.

5.3.2 Evolution mechanisms for spatter

From the single layer melt track experiments, we observed two different spatter mechanisms during LAM. At the onset of the single layer melt track experiments, the powder spatter ejected in a vertical direction, and its ejection angle altered from vertical to an inclined angle as the melt track extends towards the bottom of the powder bed. Our real-time observations on powder spatter shared many similarities to what has been reported by prior studies\textsuperscript{51,208–210}. Our results show that the laser-induced vapour jet created a recoil pressure normal to the melt track surface, ejecting powder in the material free zone (Figure 46). The material free zone is in an inverse bell shape and contains a high concentration of metal vapours (Figure 46a).\textsuperscript{210} The high-temperature metal vapours indirectly heats the surrounding argon gas and creates a convection or inward argon flow within the zone, resulting in vapour-driven powder entrainment.\textsuperscript{208,209} We clearly see that no more powder spatter was evident once the material free zone established, however, the vapour-driven powder entrainment promoted the extension of the melt track. This confirms that the vapour-driven powder entrainment is a key track growth mechanism.

During an overhang build, the melt track was extending towards the bottom of the powder bed rather than extending in a horizontal direction due to spatter ahead of the laser-matter interaction zone. The growth rate of the melt track became slower than the scan speed of the
laser beam. As a consequence, the laser beam created molten pools ahead of the melt track. This shifted the powder-free zone from the main melt track (Figure 46a) to the first newly formed molten pool (Figure 46b), such that, powder particles and melt droplets formed by subsequent melting located inside the material free zone would be ejected (Figure 46b). We clearly see that the amount of spatter increased as the melt track extended towards the bottom of the powder bed. The spatter may land onto the melt track and increase the surface roughness of the melt track. Otherwise, it lands on the powder bed and causes an uneven powder thickness, leading to a build failure. These observations elucidate why it is difficult to produce overhang features during LAM. Future studies should focus on new laser scanning strategies for overhang builds.

Figure 46: Schematics show the effects of laser beam position in the melt track on spatter. a, formation of powder spatter when laser beam is positioned inside the melt track and b, formation of powder and droplet spatter when laser beam is positioned outside the melt track.

5.3.3 The roles of pore bursting to molten pool dynamics

Figure 47 highlights key observations during LAM of a second layer melt track (L2). The laser beam produces a keyhole that penetrates through L2 and re-melts the top surface of L1 (Figure 47a). Laser re-melting promotes pore transport in the molten pools, allowing gas pores to escape into the atmosphere through a keyhole (via the same mechanism depicted in L1). For gas entrainment to take place, these pores must locate ca. 1.1 mm from the powder bed surface (based on our setup). Below this depth, laser re-melting can only generate a small amount of liquid metal that partially fills the pre-existing pores via liquid feeding (green dotted circles in Figure 47a). We hypothesise that the oxide films at the pore surface act as a physical barrier and restrict the melt flow to entrain or eliminate pores. Louvis et al. and
Olakanmi et al.\textsuperscript{72} emphasised that unless the oxide film was vaporised, it would remain in the molten pool and promote pore formation.

**Figure 47b** reveals a new formation mechanism of an open pore during LAM. At 7 ms, the laser re-melts the surface of L1 and forms a liquid bridge (indicated by purple dotted lines). Between 10 and 34.8 ms, the laser beam causes the liquid bridge to double its size while accelerating its internal melt flow, which promotes pore coalescence, growth, and transport. By 34.8 ms, the Marangoni-driven flow entrains gas pores towards both ends of the liquid bridge which significantly weakens the structural integrity of the liquid bridge. We hypothesise that laser re-melting raises the temperature of the surrounding material near the pore, indirectly heating the gas particles (see red dotted arrows). As a result, it induces a gas expansion which exerts an outward pressure at the gas-liquid interface, \textit{i.e.} causing an indirect laser-driven gas expansion. Once the gas pressure exceeds the surface tension of the liquid bridge, the weakest links (or both ends) of the liquid bridge rupture at 35 ms, and then the liquid bridge becomes a stream of liquid metal ejecting in a vertical direction at 36 ms, \textit{i.e.} forming a droplet spatter. Consequently, the closed pore burst opens, leaving a dent or crater at the surface of the melt track, also known as an open pore. Based on our observations, there are no visible laser re-melting features at the bottom of the pore until 40 ms (orange dotted circle in **Figure 47**). This indicates that spatter took place before the formation of an open pore. We postulate that metal vaporisation did not contribute to the formation of droplet spatter and open pore, dissimilar to the hypotheses depicted by reference studies\textsuperscript{208–210}. Our observations confirm that the formation mechanism of open pores is by insufficient liquid feeding, a mechanism proposed by Qiu \textit{et al.}\textsuperscript{144}. However, our results disagreed with their hypothesis on the formation of open pore was due to incomplete laser-re-melting.

**Figure 48a** shows the evolution of a third layer melt track (L3) in B2. Similar to L2, the laser beam melts the powder above the open pore and forms a liquid bridge which temporarily closes the open pore. Similar to L2, the laser beam causes an indirect laser-driven gas expansion inside the pore which overcomes the strength of the liquid bridge, resulting in pore bursting, followed by the formation of an open pore and droplet spatter. This clearly shows that pore bursting is a key formation mechanism of droplet spatter and open pores. By 34 ms, the Marangoni convection causes the liquid metal to flow in the opposite of the laser scanning
direction, showing a possible mechanism for pore closure. Most of L3 has undergone laser re-melting which removes many large pores inside the melt track but also introduces many type I pores. We hypothesise that the oxide films at the pore surface are disrupted into small pieces during laser re-melting; however, they remain inside the molten pool and act as pore nucleation sites.

Figure 47: Times-series radiographs showing LAM of a second layer Invar 36 melt track (L2) by a power of 150 W and a scan speed of 5 mm/s. a, Snapshots of the LAM process at t = 20, 460 and 680 ms. The red box highlights a region of interest (ROI). b, The ROI reveals a new pore formation mechanism, wherein an open pore was formed after droplet spatter. Red arrows indicate gas expansion. Purple dotted lines highlight the region of the liquid bridge. Orange dotted circles highlight laser re-melting takes place at the bottom of the gas pore after spattering.

Figure 48b reveals a pore healing mechanism during LAM. The laser beam penetrates through L3 and opens up a pre-existing pore. The internal gas expands radially from the porosity inside the melt track, pushing the liquid metal upwards. After that, the liquid metal swirls back into L3 owing to its high surface tension (indicated by dotted red arrows), and consequently, it heals the pore opening. During pore healing, the liquid metal flows inward, forming centrifugal Marangoni convection instead of following the centripetal Marangoni convection. This is possibly due to the combination of surface tension and gravitational force.
acting on the liquid metal overcomes the Marangoni-driven forces in the molten pool, thus the flow direction is once altered.

Our results show that pore bursting can lead to either pore healing (Figure 48b) or formation of droplet spatter and open pore (Figure 47b). We postulate that the outcomes of pore bursting depend on the size of the pre-existing pore before laser re-melting. In our case, the diameter of the pre-existing pore in L3 is ca. 250 µm (Figure 48b) which is 3.5 times smaller than that in L2 (Figure 47b), hence the gas pressure exerted from the pore in L3 is expected to be lower than that from the pore in L2. We also postulate that the positions of gas pores inside the liquid bridge can also affect the outcomes of pore bursting at 34.8 ms (Figure 47b). However, a further study is required to determine whether there is a critical pore diameter that triggers pore healing or formation of droplet spatter and open pore during laser re-melting.

Figure 48: Times-series radiographs showing LAM of a third layer Invar 36 melt track (L3) by a power of 150 W and a scan speed of 5 mm/s. a, Snapshots of the LAM process at time t = 34, 300 and 620 ms. b, The ROI reveals a pore healing mechanism, whereby the high surface tension of the molten pool prohibited spatter ejection and induces pore healing.

5.3.4 Time-resolved quantification of molten pool geometry and porosity

The measurements of the molten pool geometry show that the track length is ca. 2 mm longer than the nominal scan length of 4 mm (Figure 49a). This is possibly due to that a molten pool was larger than the width of the BN powder bed, and thus it spreads outwards and
extends the track length. The track depth increases rapidly in L1 due to the pore formation inside the melt track, whereas it only increases up to 50 μm in L2 and L3, because the powder thickness is significantly shallower in L2 and L3 compared to that in L1. The measurements of the melt track geometry for L2 and L3 indicate that they are heavily re-melted after a successive melt track is built.

**Figure 49b** shows that L1 exhibits the highest overall area shrinkage of 3 %, whereas L2 and L3 exhibit an overall area shrinkage of 2 %. Since L1 is formed under an overhang condition, the effective thermal conductivity of the powder bed is ca. one hundredth than that of a solid substrate\(^\text{277}\), the heat transfer in L1 is slow, causing L1 to maintain at a high temperature throughout LAM. Conversely, L2 and L3 are built on top of another solid track, which acts as a heat sink, therefore L2 and L3 cool much faster than L1. Given that the volume expansion and material shrinkage are directly proportional to the temperature of the AM part, L1 is expected to achieve the highest volume shrinkage. The area shrinkage measurements of L3 fluctuate ups and downs compared to that of L1 and L2, because L3 has undergone re-melting, so that it constantly expands and contracts during LAM.

**Figure 49c** shows that the changes of porosity (%) during B2. L1 exhibits a maximum porosity of 27% at 125 ms because a large pore (with a diameter of ~ 1 mm) is formed at the front of the melt track (**Figure 47**). As the melt track extends, only small pores (with a diameter of < 0.5 mm) are formed, resulting in a significant drop in porosity from 27 % to 8 %. When the closed pore in L2 transforms into an open pore due to pore bursting and spatter formation, the porosity drops from 8 % to 6 % at 30 ms. This is supported by the fact that the porosity quantification does not take open pores into account. After that, the porosity of L2 and L3 remains ca. 3 % because the total porosity is small compared to the volume of the melt track.
Figure 49: Time-resolved quantification of melt features in B2: a, length and depth, b overall area-shrinkage and c, porosity.
5.3.5 *Posteriori* XCT analysis

Based on the spatial resolution of the synchrotron X-ray imaging setup, we are unable to quantify any pores with a diameter less than 20 µm. Hence, we performed high-resolution XCT scans to examine both melt tracks, visual their melt track morphology and also quantify the pore size distributions in 3D.

*Figure 50a* shows that the melt track produced from a virgin powder exhibits a porosity of 0.08%. Based on the resolution of the XCT data, the melt track exhibits no open pore but it contains some closed pores with an average equivalent diameter \(d_{\text{avg}}\) of 10 µm. *Figure 50b* shows that the melt track produced from an oxidised powder has a total porosity of 15.1% in which 6.5% is closed pores and 8.6% is open pores. Remarkably, the measurements of closed pores by XCT and by synchrotron X-ray radiography matched reasonably well.

The largest closed pore in B1 has a \(d_{\text{avg}}\) 73 µm, whereas \(d_{\text{avg}}\) of the largest closed pore and open pore in B2 are 535 µm and 609 µm, respectively. The normalised frequency graphs (*Figure 50c*) show that both tracks exhibit a significant amount of small pores with a \(d_{\text{avg}}\) of 10 µm. We postulate that they are mainly gas pores (type I pores) due to their small sizes. In contrast, the cumulative frequency graphs show that there are fewer but larger pores in B2 than those in B1, suggesting that the presence of oxide films in the molten pool promotes pore formation and possibly pore growth during LAM.
Figure 50: 3D volume rendering of melt tracks of from a, virgin (B1) and b, oxidised Invar 36 powders (B2). c, Their pore size distributions.

5.4 Summary

In this study, we performed LAM of virgin and oxidised Invar 36 powders under overhang and layer wise build conditions using in operando X-ray imaging and a LAM process replicator (LAMPR). We have revealed new observations on the formation of spatter, porosity and the powder free zone.
Our results confirm that the molten pool wetting and vapour-driven powder entrainment are key track growth mechanisms for LAM. The presence of oxide films in the molten pool alters the temperature coefficient of surface tension of Invar 36 from negative to positive, altering the Marangoni convection from an outward centrifugal to inward centripetal flow. The oxides form physical barriers that restrict the gas transport and also act as nucleation sites for porosity formation.

There are two types of pores in the melt tracks: Type I gas pores have a diameter less than 250 μm, a low solubility, and high buoyancy in the liquid metal whereas (type II) pores have a diameter greater than 250 μm and their surfaces are covered with a thin oxide layer. They can also be formed by coalescing type I pores.

Laser re-melting could disrupt the oxide layers inside the molten pool/melt track, promote gas transport, allowing gas pores to escape into the atmosphere via a keyhole. It also reduces the size of pre-existing pores if these pores located within the laser penetration depth of ca. 1.1 mm. Otherwise, pores are partially filled by insufficient liquid feeding, changing them from a spherical to an irregular shape.

Notably, we uncover a new phenomenon, pore bursting, during LAM. It has two very different outcomes: (1) promoting pore healing via liquid feeding or (2) inducing open pores via the formation of droplet spatter. This demonstrates droplet spatter can be formed by indirect laser-driven gas expansion inside the melt track as well as the laser-induced vapour jet at the melt surface.

In addition to qualitative analysis, we have quantified the changes in melt track geometry, porosity and shrinkage during LAM, combined with 3D visualisation and quantification of porosity by posteriori XCT. These aforementioned quantifiable can be used to develop existing process simulation tools for the prediction of geometry and morphology of the melt track.
Chapter 6 :
Conclusions

A custom-built laser additive manufacturing process replicator (LAMPR) was developed and combined with high-speed synchrotron X-ray imaging to investigate the laser-matter interaction and powder consolidation phenomena during LAM. Three materials were examined under an overhang configuration: SS316L, 13-93 bioactive glass and Invar 36. These investigations elucidated the underlying phenomena behind the formation of melt tracks, denuded zone, and defects, including spatter and porosity. In addition, the effects of impurities and oxide films on LAM were postulated.

The results suggested that the alloy powders absorbed the laser energy at their surfaces, transferring the energy to the rest of the powder bed via heat conduction. The 13-93 bioactive glass powder absorbed the laser energy owing to the presence of transition metal oxides (TMOs). The TMOs re-radiate the absorbed laser energy as heat energy; the heat energy is transferred to the rest of the 13-93 bioactive glass powder via a phenomenon known as radiation conduction.

The formation of metallic melt tracks was driven by molten pool wetting and vapour-driven particle entrainment. This was observed for all build and powder conditions investigated. In contrast, the formation of the 13-93 bioactive glass track was primarily driven by viscous flow.

A distinct fluid flow behaviour was observed in LAM of an oxidised Invar 36 powder as compared to the Invar 36 virgin powder. The in situ radiographs revealed that the Marangoni convection altered from an outward centrifugal to an inward centripetal flow owing to the presence of oxide film in the Invar 36 molten pool. The Marangoni-driven flow in the molten pool of SS316L and Invar 36 promoted pore transport and gas release into the atmosphere whereas the viscous flow behaviour of the 13-93 bioactive glass restricted pore transport and
facilitated pore coalescence, forming large closed pores. Notably, the oxides in metallic powders restricted pore transport and promoted pore growth.

Spatter is conventionally thought to be unavoidable in LAM. The results show that no spatter was found when LAM of a high viscosity material (e.g. 13-93 bioactive glass) whereas a considerable amount of spatter was formed when LAM of a low viscosity material (e.g. SS316L and Invar 36). This suggests the reduction of viscosity in the molten materials is a possibly way to design new materials to avoid spatter formation in LAM.

This thesis also presents two detailed real-time *operando* studies of layer wise LAM, elucidating the underlying phenomena behind the interactions between two or more melt tracks. Laser re-melting promoted pore dissolution in the molten pool and gas release from a keyhole, resulting in a reduction of pore size and number density for pores located within the laser penetration depth. For pores located beneath the laser penetration depth, laser re-melting only partially filled the pre-existing pores, making their shape more irregular. Notably, the larger the laser re-melting zone, the slower the molten pool cools, providing more time for gas pores to reappear and disperse across the melt track.

This thesis uncovered a new mechanism - pore bursting. Pore bursting occurred when the gas pressure of a pre-existing pore overcame the strength of the surrounding material during LAM. This phenomenon could result in two very different outcomes: (1) promoting pore healing via liquid feeding, (2) promoting the formation of spatter and open pores. However, the threshold pore size that triggers these outcomes remains to be determined. Pore bursting is an important observation because it proves that the droplet spatter can be formed by expanding gas pores via indirect laser heating, *i.e.* laser-driven gas expansion, instead of forming spatter by the laser-induced metal vapour. This is a new twist in the existing theory of spatter formation in LAM.

In addition to qualitative analysis, the changes in the melt track geometry (*e.g.* length and width), shrinkage (%) and porosity (%) during LAM were quantified. Other image analysis tools were developed to track the movements of spatter and porosity for determining their flow
velocities and directions. These results provided a better understanding of the molten pool dynamics and crucial information to develop new simulation models.

Finally, a mechanism map was used to provide new insight into the dynamic changes in melt track behaviour across a range of process parameters, e.g. improved molten pool wetting with increasing power and the morphological transition from a semi-cylindrical track to a series of spherical or ellipsoidal molten beads as scan speed decreases.
Chapter 7:

Future work

The thesis presents three detailed studies of laser-matter interaction, molten pool dynamics, and defect evolution during laser additive manufacturing (LAM) captured using synchrotron X-ray radiography. However, these studies did not provide insight into the temperature of the molten pool or melt track during LAM. I believe that the temperature measurements are crucial to elucidating the thermophysical phenomena occurring in LAM. In particular, the temperature field would help understand the following three phenomena that control the spreading of molten pool, including: 1) viscous dissipation, 2) surface tensions forces, and 3) solidification.

The future work would require the combination of in situ and operando studies of LAM using a combination of X-ray imaging, high-speed optical imaging (> 10,000 fps) and thermography (> 1500 fps). The goal is to capture the temperature field and detailed thermophysical phenomena occurring inside, at, and above the powder bed. These new observations would help us to improve our understanding on the morphological transition from a hemi-cylindrical track to spheroidisation of metal beads (due to balling).

Using these temperature measurements and existing thermophysical property databases\textsuperscript{137}, it is possible to calculate the thermophysical properties of the processing materials, including its density, dynamic viscosity, surface tension, etc. These calculated thermophysical properties can then be used to estimate the solidification and spreading times of the melt track with respect to the laser process parameters which are essential for the development of existing thermal simulation tools for LAM. In addition, they can also help developing a dimensionless mechanism map to predict track geometry, morphology and defects in LAM. Moreover, these new observations would also reinforce what has been reported in this thesis, such as the evolution mechanism of the porosity and spatter, e.g. the open pore formation.
The images from X-ray, optical and IR imaging can combine to reconstruct quasi-3D images of the molten pool / melt track over time. They can be used to verify and validate existing process simulation models that predict melt track geometry with respect to process parameters.

Henceforth, the laser additive manufacturing process replicator (LAMPR) will require an upgrade. LAMPR version II will be equipped with a new powder hopper that can perform automatic powder spreading, a moveable platform for a multi-layer build, and an oxygen sensor (with a temperature probe) for oxygen monitoring inside the chamber. In addition, LAMPR II would require several new imaging ports that enables multi-modal imaging of LAM, in real and reciprocal spacing. It will also be equipped with multi-layer build capability, such that the end-users can build AM parts with a volume of 20 mm x 20 mm x 15 mm. Therefore, these new capabilities enable scalable studies of LAM process from single layer and multi-layer builds with and without X-rays.

Once the multi-modal imaging technique becomes a mature characterisation technique, these images can be implemented to a supervised learning based machine-learning algorithm to perform automatic in situ repair of LAM parts. I believe there will also be a lot of exciting collaborations to combine multi-modal imaging with X-ray diffraction, spectroscopy and other advanced characterisation technique to acquire real-time chemical composition and structure of materials. Lastly, there will be collaborative projects with process modelling groups to feed these results generated from the multi-modal characterisation experiments for the development of next generation simulation tools to better understand, predict and control the LAM processes.
References


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Appendix I

Appendix Figure 1: Laser beam characteristics. a, measured laser power vs nominal power; b, laser scan speed vs nominal scan speed, and c, laser beam profile analysis shows the laser beam fitted by a Gaussian fitting, see colour map for the beam diameter. The full laser characteristics are given in Table 1.

The laser power was measured by two different methods as shown in Appendix Figure 1a: (1) an internal power meter of the laser system and the official R4 Laser GUI (SPI Lasers Ltd, UK), and (2) an external power meter, FL250A-SH-V1 with a Nova display (Ophir Spiricon Europe GmbH, Germany. The black line represents the nominal laser power whereas the red line represents the calibrated laser power, which is a linear fit of the measured laser powers. For the input programmed power of 100, 150 and 200 W, the calibrated laser powers are 106, 157 and 209 W, respectively.

To calibrate the length of the laser scan path, we used an embedded visible light laser beam inside the SPI laser system to scan various path lengths on an alignment screen with a 10 mm target grid (Thorlabs Inc., USA). Using such tests, we were able to adjust the X-Y scaling factor of the f-theta lens on the control software, Digistrut (Laser control system Ltd, UK). After we corrected the scan vector, we recorded the duration of each scan process using two different methods for determining the laser scan speed.
For the optical tests, we scanned two lines, a 4 mm (Optical-test1) and a 40 mm (Optical-test2), using an embedded visible light laser beam inside the SPI laser system, and simultaneously recorded the scan process at 240 fps by an iPhone6 (Apple Inc., USA). This indicated that the true laser scan speed was higher than the nominal value. To confirm this, we scanned a 4 mm line using the 1070 nm laser beam, and simultaneously recorded the scan process using a high speed camera at 1000 fps, Phantom V7.3 (Vision Research Inc., USA) with an NIR illumination source (λ = 960 nm) and a notch filter (λ =1000 nm ± 50 nm). The results agreed with the initial iPhone measurements. **Appendix Figure 1b** shows a black line represents the nominal laser scan speed whereas the red line represents the 1070 nm laser scan speeds, which is a linear fit of the measured laser scan speeds. For 5, 7.5, 10, 20 and 40 mm/s, the calibrated scan speeds are 9, 13, 17, 34 and 68 mm/s, respectively.

The laser spot size was recorded using a CCD camera with a pixel size of 3.69 μm through a unique wedge system (which consists of two quartz wedges and two NIR wedges) (Ophir Spiricon Europe GmbH, Germany). This wedge system reduced the intensity of the 1070 nm laser beam by 0.00016% to prevent the laser beam damaging the CCD camera. The beam profile was displayed using the BeamGauge software (Ophir Spiricon Europe GmbH, Germany) and the spot size was estimated by fitting a Gaussian function as shown in **Appendix Figure 1c**.
Appendix II

Appendix Figure 2: Image processing flow chart. All steps were performed by MATLAB 2016a except for the object tracking step (blue) which was performed by ImageJ.249.
Appendix Figure 3: Processed images from Appendix Figure 2. a, Raw images. b, Flat field corrected images. c, Denoise images. d, Segmented melt rack and spatter. e, Segmented pore. f, Overlaid the object boundary of (d) on (c). g, Spatter trajectory. h, Pore motion inside the melt track.
### Appendix Table 1: Laser beam characteristics of the SPI R4 laser system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Specification</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central emission wavelength</td>
<td>nm</td>
<td>1070 ± 10</td>
<td>Pass</td>
</tr>
<tr>
<td>Emission bandwidth</td>
<td>nm</td>
<td>&lt; 4.0</td>
<td>Pass</td>
</tr>
<tr>
<td>Modulation rise time</td>
<td>μs</td>
<td>&lt; 20</td>
<td>Pass</td>
</tr>
<tr>
<td>Modulation fall time</td>
<td>μs</td>
<td>&lt; 10</td>
<td>Pass</td>
</tr>
<tr>
<td>Beam diameter (Incoming)</td>
<td>mm</td>
<td>5.0 ± 0.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Beam divergence</td>
<td>mrad</td>
<td>≤ 0.45</td>
<td>0.27</td>
</tr>
<tr>
<td>( M^2 )</td>
<td>-</td>
<td>≤ 1.10</td>
<td>1.03</td>
</tr>
<tr>
<td>Circularity (%)</td>
<td>%</td>
<td></td>
<td>97.1</td>
</tr>
<tr>
<td>Eccentricity</td>
<td>%</td>
<td>≤ ± 1.2</td>
<td>Pass</td>
</tr>
<tr>
<td>Concentricity</td>
<td>mm</td>
<td>≤ ± 2.0</td>
<td>Pass</td>
</tr>
<tr>
<td>D4σX</td>
<td>μm</td>
<td>49.5</td>
<td>50.9</td>
</tr>
<tr>
<td>D4σY</td>
<td>μm</td>
<td>49.5</td>
<td>49.8</td>
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