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Enabling multi-material Molten Metal Jetting via dual-head MetalJet system

Thesis submitted to the University of Nottingham for the degree of Doctor of
Philosophy

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Abstract

Multi-material Additive Manufacturing (MMAM) enables the fabrication of integrated components with complex geometries and varied material properties. Among MMAM approaches, multi-metal AM facilitates the direct joining of dissimilar metals during fabrication and has been increasingly adopted in sectors such as aerospace, biomedical engineering, automotive manufacturing, and robotics. Established technologies such as Laser Powder Bed Fusion (LPBF) and Directed Energy Deposition (DED) have demonstrated strong industrial capabilities. However, there remains a need for alternative methods that offer high precision, process stability, and manufacturing efficiency, while avoiding the complexities of powder handling and extensive post-processing.

Molten Metal Jetting (MMJ) is an emerging droplet-based AM process that constructs 3D structures via layer-by-layer deposition of molten metal droplets. Despite its demonstrated potential in producing high-resolution and smooth-surfaced components, MMJ has so far been limited to single-material deposition.

This PhD research aims to establish the feasibility of drop-on-demand multi-metal MMJ for the first time. Key challenges in enabling multi-material MMJ lie in the absence of an available system capable of depositing two metals simultaneously, as well as a limited understanding of interfacial behaviour or process parameter adjustments for depositing metals with different melting points together.

To overcome these challenges, this study presents the development of the world's first dual-head MMJ system for multi-metal printing. A bespoke control software, implemented in LabVIEW, was designed to coordinate hardware and user interaction, achieving deposition accuracy of within 7 μm . Based on this platform, customised printing strategies were developed to produce parts with densities over 98% and electrical conductivity within 2% gap to the corresponding bulk metal. The dual-head system was subsequently used to investigate interfacial phenomena in dissimilar metal deposition. A droplet coalescence defect was identified at the interface, and novel deposition strategies were proposed and experimentally validated to mitigate this issue. This research not only provides a robust platform for future multi-material MMJ studies but also contributes fundamental insights into interfacial bonding and process optimisation essential for reliable, defect-free multi-metal printing.

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Publishments and conferences

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Abbreviation list

AM	Additive Manufacturing
Ag	Silver
Au	Gold
BSE	Backscattered Electrons
CJ	Continuous Jetting
CT	Computed Tomography
Cu	Copper
DED	Direct Energy Deposition
DoD	Drop-on-Demand
EDM	Electrical Discharge Machining
EDX	Energy Dispersive X-ray
FDM	Fused Deposition Modelling
FGMs	Functionally Graded Materials
FIB-SEM	Focused Ion Beam Scanning Electron Microscope
FPGA	Field Programmable Gate Arrays
IMCs	Intermetallic Compounds
In	Indium
LIFT	Laser-Induced Forward Transfer
LPBF	Laser Powder Bed Fusion
MHD	Magnetohydrodynamic
MMJ	Molten Metal Jetting
MMAM	Multi-material Additive Manufacturing
ML	Machine Learning
Ni	Nickel

<i>Oh</i>	Ohnesorge number
PC	Personal Computer
PID	Proportional Integral Derivative
ROI	Region of Interest
RPC	Reaction Product Control
SE	Secondary Electrons
SEM	Scanning Electron Microscope
Sn	Tin
Ti	Titanium
VI	Virtual Instruments
VoF	Volume of Fluid
WC2	Tungsten Carbide

Nomenclature

Symbol	Description	Unit
CaliX / CaliY	Calibration offset calculation in X and Y directions	μm
d_1	Deposition error at nozzle-substrate distance of 1mm	μm
d_2	Magnified deposition error after printhead angle and height changed	μm
d_s	Droplet spacing	μm
$d_{s\text{opt}}$	Optimal droplet spacing	μm
d_{s-X}	Droplet spacing in X direction	μm
d_{s-Y}	Droplet spacing in Y direction	μm
$d_{s\text{opt}}$	Optimal droplet spacing	μm
E_{slice}	Error of slicing	μm
E_{mtd}	Error of pattern alignment method	μm
E_{pst}	Error of pattern alignment position	μm
E_x	Error along X axis in multi-material deposition	μm
f	Frequency of the jetting	Hz
I_l	Current measurement of the sample	A
$\dot{j}_c$	Change rate of acceleration	m/s^{-3}
L	Effective length of resistance measurement	m
P_c	Pressure of cavity	Pa
P_g	Pressure of gas	Pa
R_a	Roughness average	μm
R_z	Surface peak-valley distances	μm
S	Area of the cross-section of the sample	m^2
t_a	Acceleration rate stable time	s
T_d	Droplet temperature	$^{\circ}\text{C}$

t_j	Acceleration rate change time	s
T_m	Melting point	°C
T_s	Substrate temperature	°C
U_1	Voltage measurement of the sample	V
V_{print}	Velocity of the stage movement during printing	mm/s
We	Weber number	
w_1	Width of the gap in Sn-In configuration	μm
w_2	Width of the gap in In-Sn configuration	μm
X_a	Acceleration distance of linear stages	mm
X_{bmp}	Empty length at the beginning of the trace	mm
X_{cali}	Calibration offset of the printhead	mm
$X_{\text{grid}}/Y_{\text{grid}}$	X/Y coordinate value of the calibration pattern (relative)	mm
X_{len}	Desired printing trace length	mm
$X_{\text{ph}} / Y_{\text{ph}}$	Position of printhead in X/Y direction	mm
X_{rp}	Relative position of the pattern	mm
X_{start}	Start position of the toolpath	mm
X_{tof}	Stage movement during the time of flying of a droplet	mm
X_{tot}	Total distance of a toolpath	mm
α	Angle between the camera coordinate and the linear stage coordinate	°
ρ	Density	kg/m ³
σ	Surface tension	N/m
σ_{LV}	Surface energy of liquid	N/m
σ_{SL}	Surface energy of solid-liquid	N/m
σ_{SV}	Surface energy of solid	N/m
σ_{R}	Electrical conductivity	10 ⁶ /Ωm

θ	Contact angle	◦
θ_Y	Contact angle of droplet in non-reactive wetting model	◦
θ_1 / θ_2	Contact angle of dissolutive wetting model, the θ_1 is the angle above the substrate while the θ_2 is the one below it	◦

1 Introduction

This chapter introduces the motivation, scope and objectives of the thesis and places the work within the broader context of Multi-Material Additive Manufacturing (MMAM). It also outlines the specific challenges addressed in this research and previews the chapter organisation that follows.

1.1 Background

Traditional manufacturing methods are typically designed for producing single-material components. To produce multi-material parts, the assembly and connection of individual materials are required, which usually increases the process cost. These weak points can negatively impact critical properties, including structural strength, electrical conductivity, and corrosion resistance. Moreover, the connection and assembly processes often struggle to meet the high precision and complexity required by advanced designs, thus hindering the widespread use of multi-material components in circumstances where integral, complex shape parts are required.

Additive manufacturing (AM), also known as 3D printing, offers an advanced solution by enabling the production of complex components made from one or more materials. This technology builds parts layer by layer, allowing different materials to be combined within each layer to enhance functionality or geometric complexity. In contrast to traditional manufacturing, 3D printing significantly broadens design possibilities. Additionally, compared to traditional subtractive manufacturing methods, its cost of realising design flexibility remains relatively low. This makes 3D printing particularly advantageous for creating intricate parts with multi-material needs.

In Multi-Material Additive Manufacturing (MMAM), the focus has primarily been on polymer materials due to their ease of processing and versatility. However, polymer-based parts often fall short in terms of mechanical strength, thermal stability, and electrical conductivity, which are crucial for high-performance applications. In such cases, metals offer a more suitable alternative. Current multi-metal 3D printing technologies include Direct Energy Deposition

(DED) and Laser Powder Bed Fusion (LPBF). DED works by melting metal feedstock to form a part using an energy source such as a laser or electron beam, while LPBF uses a high-powered laser to selectively melt metals in the powder bed and build a part layer by layer. These techniques have already been successfully applied to produce integrated functional parts, such as robotic arms, jet nozzles, engine casing, and medical equipment.

Besides these two processes, Molten Metal Jetting (MMJ) presents a promising alternative in AM, enabling the droplet-by-droplet construction of components using molten metals. MMJ achieves dimensional accuracy, ranging from 50 μm to 1 mm, while eliminating the need for powder handling and extensive post-processing. This simplification not only improves design flexibility but also reduces operational complexities. Even though it remains a pre-commercialised technology with a material portfolio that is not yet widely available compared to LPBF or DED, MMJ has shown its potential in building up micro-electronics such as antennas, circuits and sensors. Among the various MMJ techniques, MetalJet stands out for its exceptional accuracy of 50 μm and stable droplet generation. However, despite their promising capabilities in accuracy and availability of a diverse range of materials, MMJ techniques have not yet been explored for multi-material applications, creating a gap in their development and potential use.

To enable multi-material studies in MMJ, a system capable of printing with at least two distinct metals is essential. At the outset of this PhD, no such multi-material MMJ system had been developed. Therefore, an important step in this work was the design and realisation of a suitable MMJ platform. In addition to system development, another key focus of this research is to establish how dissimilar metals can be printed together in MMJ, ensuring proper bonding at joints. This requires a fundamental understanding of interfacial behaviour and the identification of suitable process parameters in multi-material printing.

1.2 Research aim

This PhD aims to explore multi-material MMJ printing. The following objectives have been identified to achieve this goal:

1. Develop a dual-head MetalJet system capable of depositing two distinct metals onto a single part. This will involve the design, construction, and testing of both the hardware and software components of the system.
2. Validate the multi-material printing capabilities of the newly developed system to ensure its performance and precision in handling dissimilar materials.
3. Characterise the interfaces between the dissimilar metals, gaining a deeper understanding of the mechanisms behind interface formation to ensure strong, reliable bonding between the materials.

1.3 Thesis structure

The result of this PhD is demonstrated in three stages: system development, printing strategy design and multi-material study. The chronological order of work is shown in Figure 1.1.

The chapters of the thesis are outlined as follows:

Chapter 2: Literature Review provides essential background knowledge for studying multi-material MMJ from three key perspectives. First, it presents an overview of advancements in MMAM. Then, it offers a comprehensive analysis of current MMJ systems. Finally, recent developments in MMJ are discussed, establishing a foundation for further multi-material research in the field.

Chapter 3: Materials and Methods details the equipment, materials, experimental procedures, and characterisation methods used in this study. This chapter outlines the experimental plans for system evaluation, printing strategies, and the study of multi-material interfaces.

Chapter 4: System Development Evaluation is the first results chapter, focusing on the design and development of both the hardware and software

components of the system. It includes initial test results and troubleshooting processes. Two initialise tests were conducted, using tin (Sn) and silver (Ag), representing materials with low melting points and high melting points. The chapter also evaluates the system's accuracy, providing the necessary groundwork for the subsequent analysis.

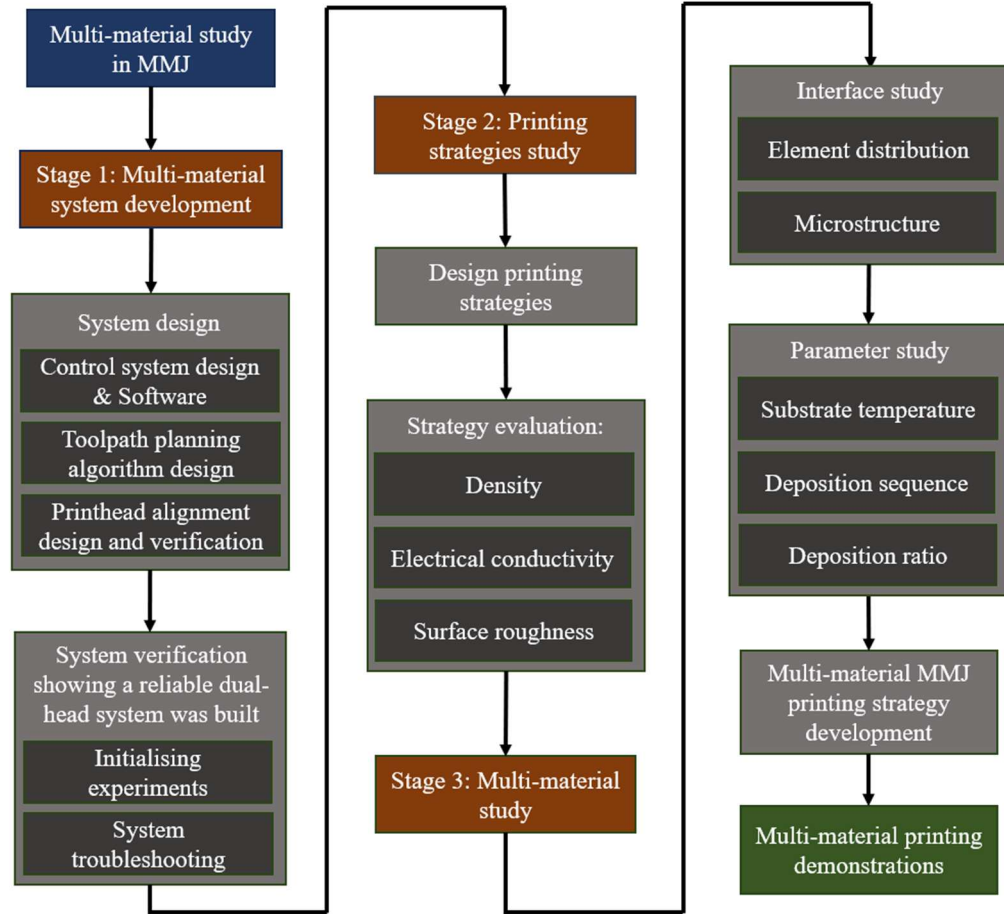


Figure 1.1 Flow chart showing the process of research during this thesis

Chapter 5: Investigation on Printing Strategies builds on the previous chapter by examining the effects of various MMJ printing strategies on the density, electrical conductivity, and surface roughness of the final parts. Special printing strategies were also developed to achieve pore-free printing with the MetalJet system.

Chapter 6: Sn-In Multi-material Study presents research on the multi-material printing of Sn and indium (In). Droplet-by-droplet samples were fabricated using these two materials. The chapter evaluates multi-material

deposition accuracy, explores interface formation, and investigates key printing parameters such as substrate temperature and deposition sequence. The impact of deposition ratio is also examined. At the end, an interdigitated structure built by Sn and In was demonstrated to show the multi-material capability of the system.

Chapter 7: Conclusion and Future Work summarises the key findings of the PhD research, highlighting how the study advances the field of multi-material MMJ. The chapter concludes with a discussion on future work, identifying areas that have not been fully addressed in this thesis.

1.4 Research gaps

A review of the current literature on MMJ, alongside developments in multi-material capability in other metal AM methods such as LPBF and DED, reveals that multi-material MMJ remains largely unexplored. This gap is primarily due to the absence of an available multi-material MMJ system. Existing MMJ machines are limited to a single printhead, which restricts experimental investigation. However, moving from single-material to multi-material MMJ is not merely a matter of adding a second printhead. A dual-head system requires advanced control software capable of managing independent temperature control for each head, seamless switching between heads, and precise alignment calibration. It also demands a more complex and challenging process of troubleshooting and system tuning. The addition of a second printhead, together with printhead switching and alignment calibration, introduces new sources of positional error that can accumulate and compromise the accuracy of the final multi-material print.

Beyond the hardware challenge, there is a lack of research into the interface formation between dissimilar materials in MMJ. While alloying at the interface can be inferred, the width of the fusion zone and the likelihood of droplet coalescence cannot currently be determined through modelling or calculation. Existing simulation models are unsuitable, as alloying introduces dynamic changes in composition and temperature during solidification. Furthermore, knowledge from single-material MMJ cannot reliably be applied to predict how

printing parameters such as nozzle temperature and substrate temperature, or the use of different substrate materials, will affect the interface in multi-material builds. As a result, determining the optimal parameters for printing dissimilar metals using MMJ is not yet feasible.

1.5 Statement of novelty

This PhD thesis explores the multi-material printing in MMJ using a newly developed dual-head MetalJet system. Tailored printing strategies of MMJ have been developed, and interface formation between droplets of dissimilar materials was studied. It also investigates, for the first time, the effects of substrate temperature, deposition sequence, and deposition ratio on the interface quality. The key contributions of this research are as follows:

1. Development, setup, debugging, and troubleshooting of the dual-head MetalJet system.
2. Creation of a multi-material printing process tailored for the dual-head system, including nozzle heating, printhead alignment and dual-head printing.
3. Introduction of a novel high-precision printhead alignment methodology using image-based feedback and calibration algorithms for multi-material MMJ printing.
4. Design and evaluation of printing strategies of droplet packing to optimise MMJ performance.
5. Characterisation of the microstructural interface formed between Sn and In droplets using Scanning electron microscope (SEM) and Energy dispersive X-ray (EDX) mapping.
6. Analysis of how substrate temperature and deposition ratio (droplet number ratio between two materials) affect interface formation, focusing on elemental distribution, pore formation, geometric and compositional continuity via SEM and EDX.
7. Development of a printing strategy enabling void-free, geometrically continuous Sn–In interfaces for gapless multi-material printing, validated by SEM characterisation.

These advancements provide new insights into the challenges and possibilities of multi-material Molten Metal Jetting, contributing to the broader field of additive manufacturing.

2 Literature review

As the aim of this PhD research is to explore the multi-material printing in MMJ, the literature review aims to identify the research gaps between the current state of MMJ process to achieving MMAM. An understanding of the development and current state of both multi-material additive manufacturing and MMJ is essential.

The literature review is divided into four main sections. The first section provides an overview of multi-metal AM methods and their applications. The second section delves into the MMJ technologies, covering actuation methods and setups, process study, materials development and applications. Finally, the review will identify and discuss the gaps in extending MMJ into the multi-material domain.

2.1 Current state of the art in multi-metal Additive Manufacturing

AM is an advanced technology that creates three-dimensional structures by building up materials layer by layer. In contrast to traditional subtractive methods, AM not only significantly reduces material waste but also enables the efficient production of complex geometries, thereby shortening product development cycles [1]. MMAM involves the use of two or more distinct materials in a single part, allowing for the integration of multiple properties such as wear resistance, corrosion resistance, high electrical conductivity, and high thermal conductivity [2]. MMAM initially focused on polymers and has been realised through techniques such as Fused Deposition Modelling (FDM), Polyjet, and Inkjet [3]. This approach has found widespread application across various industries, including aerospace for lightweight composites, healthcare for rehabilitation assistive soft robots, bioscience for microfluidic devices for cell research and electronics for wearable devices [1], [4], [5]

However, polymer-based materials find it hard to meet the demands of parts operating in extreme environments, such as high temperatures, heavy loads, and intense vibrations. The electrical and thermal properties also fall short for many

functional devices like batteries, thermocouples, motors or heat sinks [3]. On the other side, metals offer superior mechanical properties, heat resistance, electrical and thermal conductivity compared to polymers, making MMAM an area of growing research interest [2], [3], [6].

This chapter explores existing multi-metal AM technologies and their applications. The chapter focuses on multi-metal AM technologies, detailing the optimisation and design of these processes to accommodate multi-material printing. The advantages, limitations, challenges and suitable applications of different processes will also be addressed. Then, the causes and mitigation of interface defects in current multi-metal AM processes will be discussed. This will serve as a foundation for predicting and understanding what happens at the interface in multi-metal MMJ.

Currently, two mainstream processes are employed for fabricating parts with dissimilar metals, utilising various energy sources to melt and combine the metals. These processes are DED and LPBF [5], [7]. Another emerging metal AM process, named Laser-Induced Forward Transfer (LIFT), also shows its capability in MMAM. Three sub-sections are used to outline the principles underlying each of these technologies and discuss the enhancements that have been developed to facilitate multi-material printing.

2.1.1 Multi-material Laser Power Bed Fusion (LPBF)

Multi-material LPBF is a variant of LPBF adapted to enable the fabrication of components containing more than one metallic material. This section reviews the state-of-the-art in this area, covering both the technical methods developed for achieving multi-material printing with the resulting interface characteristics and defects.

2.1.1.1 Multi-material LPBF Methods

LPBF employs a focused laser beam directed through a series of mirrors to scan and selectively melt layers of metal powder on a powder bed, constructing 3D components layer by layer, as illustrated in Figure 2.1(a) and (b) [8], [9]. LPBF typically ensures a printing accuracy of 100 to 800 μm , depending on the

printing parameters and algorithm applied [10], [11], [12]. Recognised as a mature technology in the field of metal AM, LPBF has been commercialised and is capable of processing a broad range of materials, including metals, alloys, and ceramics [12].

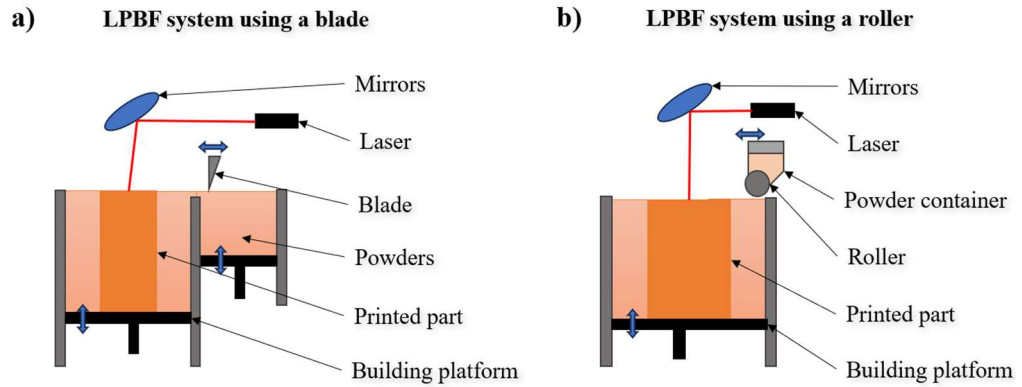


Figure 2.1 Schematic of blade mode and roller mode LPBF systems

For multi-material applications, the technique of spreading multiple powders on the bed prior to laser scanning is fundamental to LPBF. The first approach is to dispense mixed powder layer by layer, as depicted in Figure 2.2(a), where a motor-assisted vibration chamber was used to mix up powders of dissimilar materials [13]. Although it is feasible to generate layers with varying compositions by pre-mixing or dynamically mixing powders, modifying the composition within individual layers presents challenges. To address these, in the second approach, ultrasonic vibration and electrostatic-pneumatic methods were designed to dispense powders with dissimilar materials separately in each layer [7]. For instance, Aconity3D utilises an electrostatic-pneumatic approach to precisely control powder placement, as shown in Figure 2.2(b). Initially, a charged roller collects the first metal powders using the electrostatic method. Then, the powders were deposited to the powder bed on demand the powder onto the bed by triggering the gas flow through the micro channel on the drum. This process is repeated with a second metal to complete the layer [14]. In another setup utilising the ultrasonic-assisted process, independent powder distribution feeders apply ultrasound to precisely control the flow of fine powder [15]. The dispensers carry the powders of dissimilar materials and deposit them onto the powder bed, as demonstrated in Figure 2.2(c). The

ultrasonic method can lead to boundary contamination due to imprecise dispensing. Improvements by Wei, et al. [16], shown in Figure 2.2(d), a vacuum sucker was applied to remove unmelted powder before a second deposition cycle to reduce powder mix at boundaries.

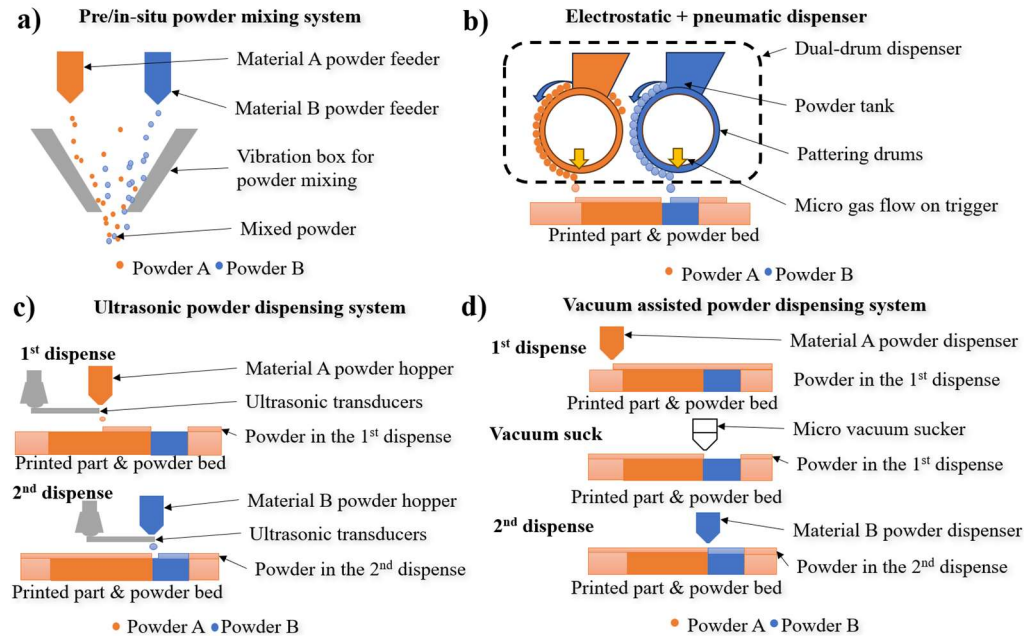


Figure 2.2 Schematic of: (a) In-situ powder mixing system, (b) Electrostatic-pneumatic powder dispenser [14], (c) Ultrasonic-assisted powder dispensing systems, (d) Vacuum-assisted powder dispensing systems.

Current research in multi-material LPBF predominantly focuses on optimising process parameters and scanning toolpath to enhance the mechanical properties of joints of dissimilar metals [7], [8], [10], [17]. Successful examples include the combination of materials such as MS1/H13, SS 316L with CuSn10, and Ti6Al4V with Inconel 718 [17]. Figure 2.3(a) and (b) illustrate sophisticated structures like a 316L/CuSn10 art piece and a turbine disk, respectively [16]. Figure 2.3(b) demonstrated a turbine disk fabricated by 316L/CuSn10 [16]. Additionally, multi-material LPBF has applications in anti-counterfeiting technologies, where intricate patterns like QR codes are embedded into materials, visible only under X-ray examination, as demonstrated in Figure 2.3(c) and (d) [18].

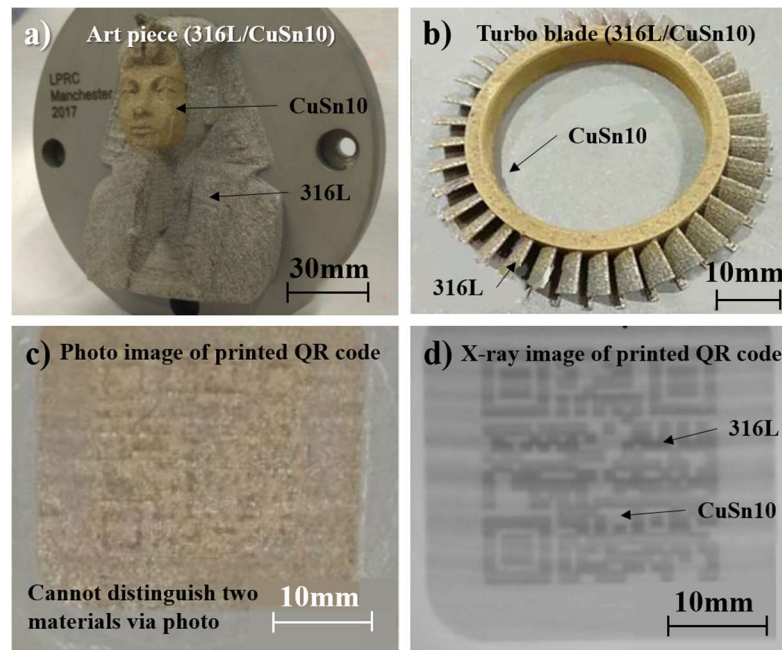


Figure 2.3 Parts fabricated by multi-material LPBF. (a) Photo of an art structure made of 316L and CuSn10, adapted from [16], (b) Photo of a turbo blade build made of 316L and CuSn10, adapted from [16], (c) Photo of an anti-counterfeiting QR code made of 316L and CuSn10, adapted from [18], (d) X-ray image of the QR code made of 316L and CuSn10, adapted from [18].

2.1.1.2 Interface microstructure and defects in multi-material LPBF

In multi-material LPBF, the interface microstructure plays a critical role in determining joint quality and overall part performance. When the energy input is sufficient and the materials have similar melting points and high mutual diffusivity, a defining feature at the interface is the formation of a fusion zone. This region typically exhibits a gradual compositional gradient between the dissimilar materials, which promotes the development of a strong metallurgical bond. [19]. For example, LPBF fabricated 300 maraging steel and 304 stainless steel joints, showing a fusion zone at a width of 120 μm [20], as illustrated in Figure 2.4, where metals on two sides are fully mixed in the interdiffusion region.

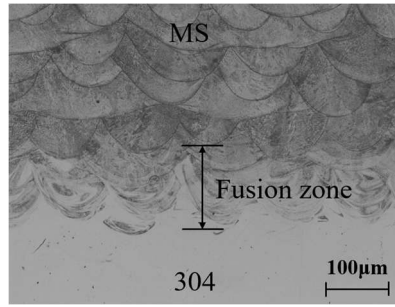


Figure 2.4 SEM image of MS/304 fusion zone by LPBF, adapted from [20].

The microstructure of the fusion zone can serve as indicators of effective bonding. For instance, the grains at the 316L/C52400 interface are finer than in the bulk materials themselves. These grain refinements, as shown in the Electron Backscatter Diffraction (EBSD) image in Figure 2.5(a), contributed to interface hardening and crack suppression [21]. Another example is that the recrystallised fine needle-shaped steel gains at 300-grade maraging steel/T2 copper interface enhanced hardness and suppressed crack formation, as illustrated in Figure 2.5(b) [22].

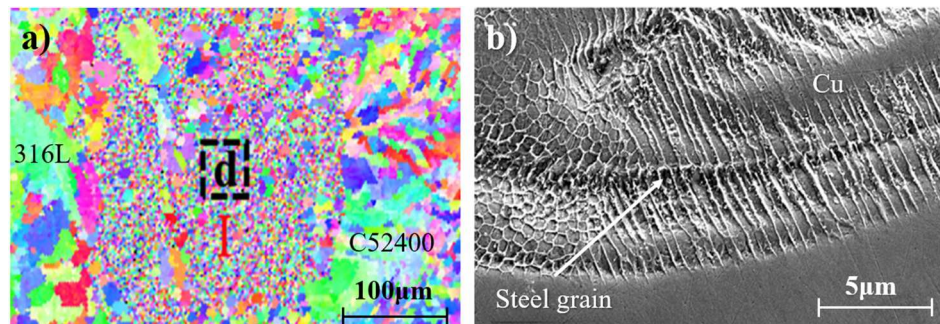


Figure 2.5 Microstructure of the fusion zone (a) EBSD image showing the grain refinement at 316L/C52400 interface, where “[d]” is the fusion zone, adapted from [21], (b) SEM image showing the needle-shaped steel grains penetrating the copper at the interface, adapted from [22].

Another indicator of bonding at the fusion zone is the flow of the Marangoni effect, with the diagram displayed in Figure 2.6(a). Figure 2.6 (b) shows the SEM image of the Marangoni effect at grade 300 maraging steel/T2 copper interface at a joint made by LPBF. Marangoni typically occurs when variations in temperature, solute concentration, or other physical and chemical changes take place, causing liquid to flow from areas of lower to higher surface tension,

thus helping mixing and diffusion during melting, contributing to bond strength in the fusion zone [9].

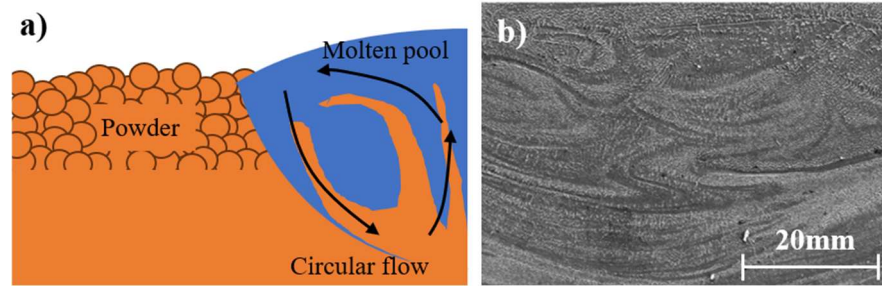


Figure 2.6 Marangoni effect in multi-metal LPBF. (a) Diagram of Marangoni flow at molten pool, (b) SEM images of microstructure caused by Marangoni flow at 300 maraging steel/T2 copper interface, adapted from [9].

At the multi-material LPBF interface, typical defects include intermetallic compounds (IMCs) formation, porosity, gaps, cracks, delamination and lack of fusion. The formation of IMCs within fusion zones presents a significant challenge [4], [7], [8]. These compounds arise from the interdiffusion and chemical reactions between metallic elements, exhibit an ordered crystal structure and properties markedly different from those of the constituent metals. Most IMCs are inherently brittle and rapid solidification in LPBF exacerbates this problem, leading to cracking and premature failure [9]. Notable example is the Ti-Al IMC at Ti6Al4V / AlSi10Mg interface [23] as shown in Figure 2.7. Several strategies have been developed in LPBF to mitigate IMC formation at dissimilar material interfaces. From the viewpoint of heat management, methods such as optimising laser energy input to reduce excessive melting [23], enhancing cooling rates to restrict diffusion-driven reactions [9] and applying tailored scanning strategies has been proven to be effective [4]. Applying interlayers to buffer chemical incompatibilities or using functionally graded transitions has also been proposed to limit harmful IMC formation [4].

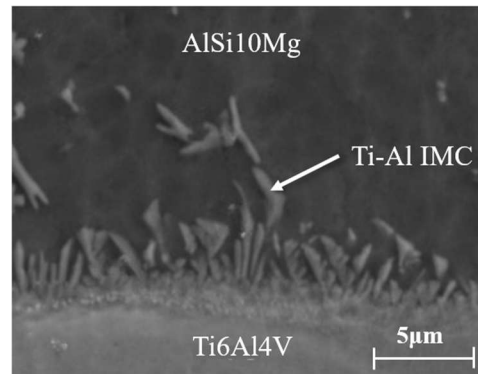


Figure 2.7 SEM image of Ti6Al4V / AlSi10Mg interface, where Ti-Al IMCs can be found, adapted from [23].

Pores and gaps formed at the interface usually occur when energy input or material compatibility is suboptimal. Insufficient laser energy can leave large pores, particularly on high reflectivity or high conductivity metals like Cu. As shown in Figure 2.8 (a), pores were observed from the SEM image of the AlSi10Mg/C1840 interface [24]. In contrast, excessive energy input can lead to overheating, which evaporates the metal and forms smaller pores [9], [25]. Both scenarios are adversely affecting joint quality. Defects of cracking and delamination are also prevalent, primarily due to mismatches in thermal expansion coefficients between the bonded metals. The difference in thermal expansion and thermal conductivity leads to residual stresses upon cooling to easily surpass the bonding strength at the interface. The crack problem can be more serious if brittle IMCs are present [26] [27]. Example of cracks at the interface are the LPBF joint of 316L/C18400 [28] and 316L/CuSn10 [19] due to the high thermal expansion and conductivity factor of copper (Cu) alloy, as shown in Figure 2.8 (b) and (c). Optimising the toolpath scanning strategy in both DED and LPBF has been reported to effectively mitigate stress-induced cracking and delamination [10].

When energy input is insufficient, especially between materials with contrasting thermal or chemical properties, unmelted boundaries may form instead of a fusion zone [8], [17]. These boundaries obstruct metallurgical bonding, typically occurring at the metal-ceramic interface rather than the metal-metal interface, as seen in steel/ZrO₂ samples, illustrated in Figure 2.8 (d) [27]. The

presence of residual unmelted particles along the interface often leads to poor mechanical integrity.

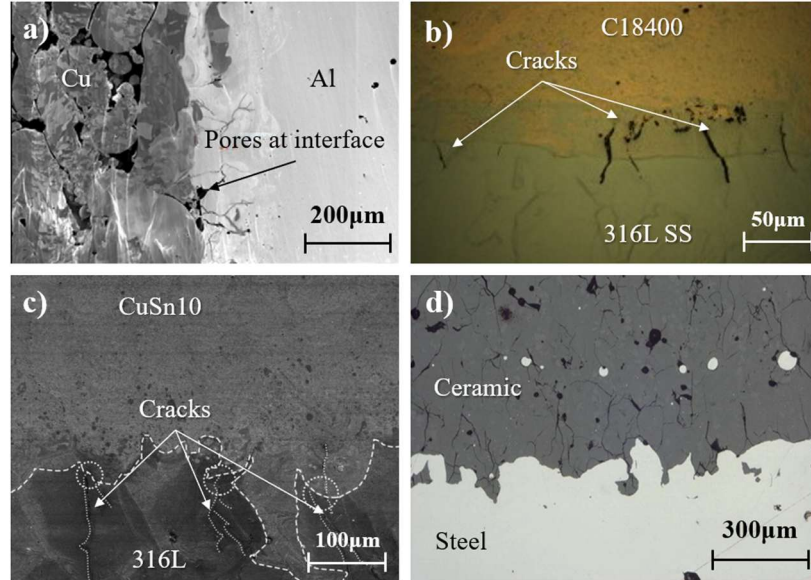


Figure 2.8 Defects at multi-material LPBF interface: (a) SEM image of the pores on the Cu side of Cu/Al interface, adapted from [24], (b) Microscope image of the cracks at 316L/C18400 interface, adapted from [28], (c) SEM image of the cracks at the 316L/CuSn10 interface, adapted from [9], (d) SEM image of the clear boundary at the steel-ceramic interface caused by a lack of interdiffusion, adapted from [27].

To address these challenges, several multi-metal connection strategies have been developed. When fabricating joints using materials with different thermal properties or poor mutual solubility, the method of adding gradient transition layers has been proven effective [9], [17]. This approach, as shown in Figure 2.9(a), introduces a transition layer with a composition gradient between the two metals, allowing material A to gradually transit to material B. The gradient layer helps to mitigate the effects of residual stress and effectively prevents cracking in multi-metal joints and suppresses the concentration of IMCs [22], [29]. In cases where direct or gradient transitions are ineffective, especially when connecting immiscible metals, a third material interface layer can be used, as displayed in Figure 2.9(b) [17]. This intermediary material serves as both a diffusion barrier and bonding link, with examples including the use of the intermediate layer of Nb/Cu to connect Inconel 718 and titanium alloys [30].

Finally, for the situations where diffusion is poor or inherently limited, the strategy of applying mechanical interlock structures at the interface was developed [8], [9], [11], [17], as shown in Figure 2.9(c). Typical designs of the interlock patterns are saw teeth and tree-shaped patterns and have been proven effective in increasing contact area at the joint and promoting mechanical stability [4], [19].

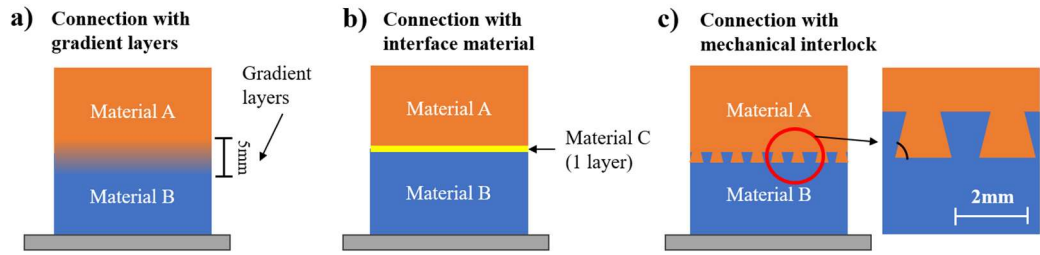


Figure 2.9 Schematic of methods for connecting dissimilar metals.

2.1.2 Multi-material Direct Energy Deposition (DED)

DED is an additive manufacturing technique where feed material is directly melted by an energy source such as a laser, electron beam, or electric arc and deposited onto a substrate or existing part to build layers and create the final shape [17], [31], [32], [33]. This process, illustrated in Figure 2.10, utilises either wire feed or powder blown with shielding gas to deliver material to the energy source's focal point at the nozzle. The molten metal forms a pool that moves with the printhead, solidifying into a trace that, when layered repeatedly, constructs a near net-shape part. DED's accuracy, typically ranging from 0.5mm to a few millimetres [31], [34], varies based on the material, energy source, and toolpath. It is particularly suited for fabricating large components and performing additive repairs [17], [31], [32], [33]. Post-processing, including heat treatment and machining, is often necessary to enhance the mechanical properties and surface quality of DED-manufactured products.

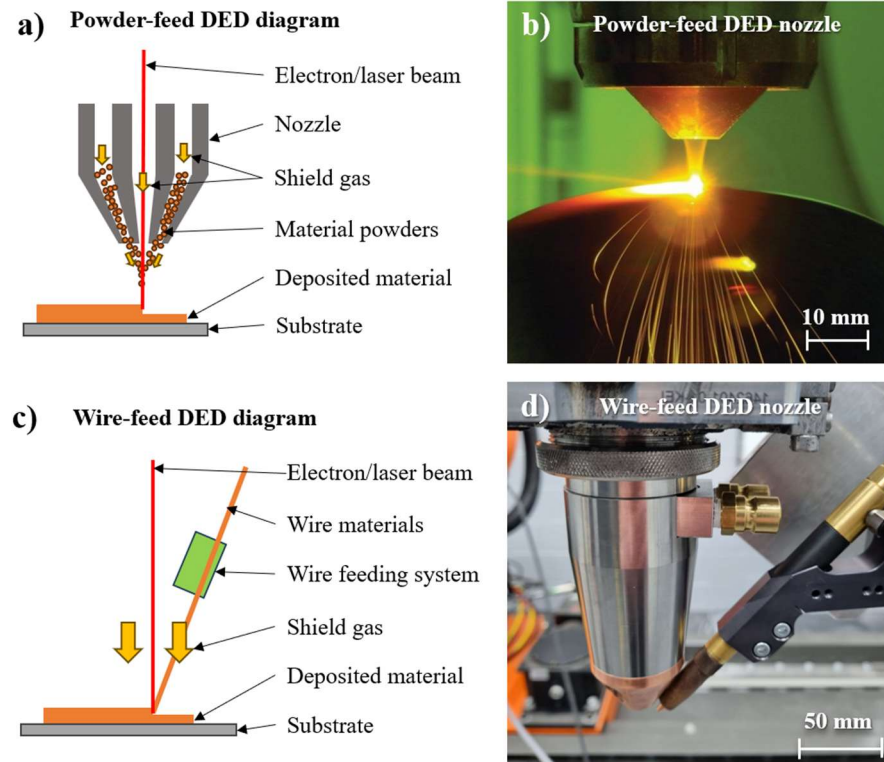


Figure 2.10 Diagrams of powder-feed and wire-feed DED system, system pictures adapted from [35], [36]

DED's capability for multi-material printing is primarily achieved through feed material modification [17], [31]. Changes in feedstock, such as switching the wire or altering the powder supply, as shown in Figure 2.11, allow for multi-material deposition. One difference between these two approaches is that powder-based DED systems allow the gradual change of feeding materials. This makes them capable of varying composition through pre-mixing or in-situ mixing of powders, which is advantageous for applications requiring composition gradient changes, such as functionally graded materials (FGMs) [6], [11], [17].

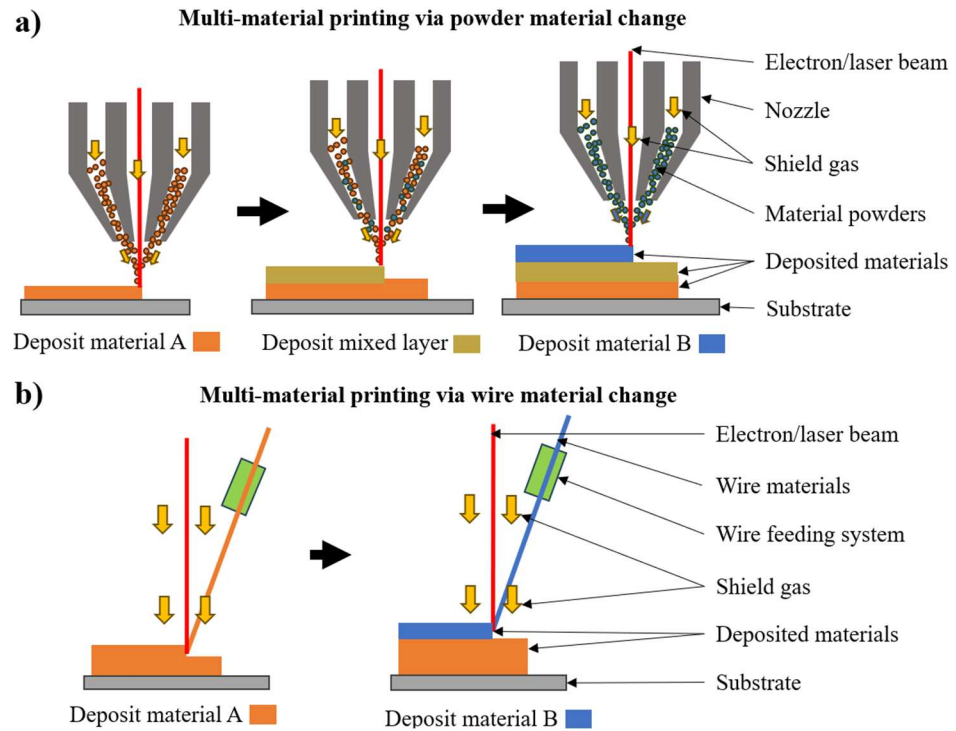


Figure 2.11 Diagrams of multi-material DED methods. (a) Powder material is being altered in the nozzle, (b) Feeding wire material change.

Research in multi-material DED has focused on creating joints between different engineering metals, including high-strength, corrosion-resistant alloys like titanium (Ti), nickel (Ni), aluminium (Al), and copper alloys. Successful examples include combinations like Cu-H13 and Ti6Al4V-Inconel 718, which demonstrate reliable mechanical strength [31], [32], [33]. In the aerospace sector, multi-material DED has been used to fabricate complex components such as rocket nozzles, as depicted in Figure 2.12(a), with the resulting multi-material rocket nozzle shown in Figure 2.12(b) [37] [38].

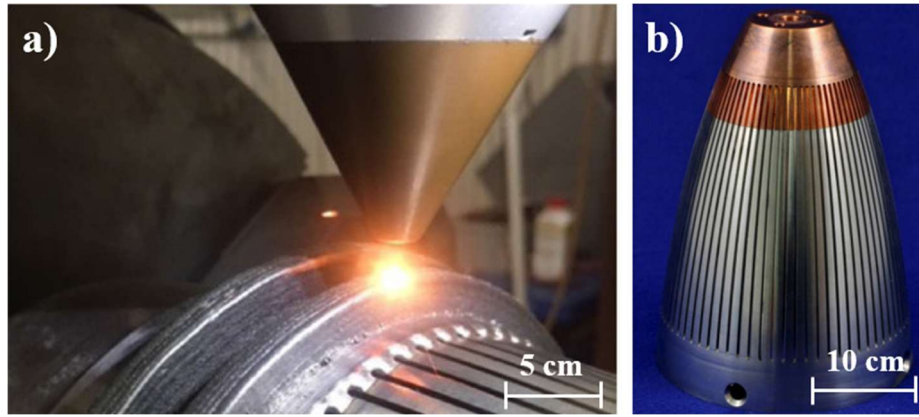


Figure 2.12 (a) Photo of a multi-material rocket nozzle in DED fabrication, adapted from [37], (b) Camera image of the DED-fabricated rocket nozzle, adapted from [38].

When sufficient energy is applied, the multi-material DED interface forms a fusion zone like LPBF. The width of the fusion zone in DED can reach a few millimetres, which is wider than that of LPBF due to its higher energy input [4]. As one of the typical defects at the DED interface, pores can be caused by uneven powder spraying, unmelted particles, rebound particles or entrained gas [4]. The micropores at the interface can do harm to the mechanical properties of the bimetallic joint. For example, Figure 2.13 (a) shows micropores at the GRCop-84/IN718 interface, respectively. The pores turned into large voids after the compression test with thermal cycling and became weak points in the bimetallic joint, as shown in Figure 2.13 (b). Cracks and IMCs are also typical defects at the DED interface, as demonstrated in Figure 2.13 (c, d) [26], [31]. The mechanisms behind the formation of cracks and IMCs in DED are similar to those observed in LPBF. Cracks typically arise when the two materials at the interface have mismatched thermal expansion coefficients or melting points. IMCs, on the other hand, are formed as new brittle phases during the interdiffusion of the constituent metals at elevated temperatures. When the input energy is insufficient, a clear boundary at the interface can be found, as shown in the interface of 316L/IN718 in Figure 2.13 (e). These kinds of joints with a clear interface boundary often indicate insufficient metallurgical bonding, which can be mitigated by reversing the deposition sequence. [29].

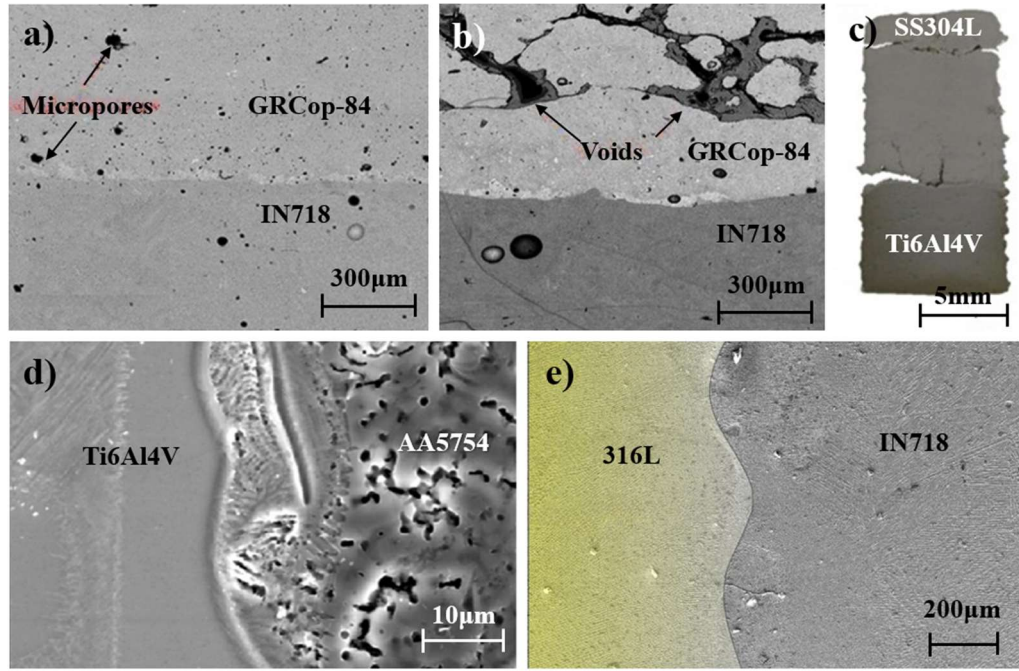


Figure 2.13 (a) SEM images of micropores observed at DED GRCop-84/IN718 interface, adapted from [39], (b) SEM images of large voids found at GRCop-84/IN718 interface, adapted from [39], (c) Microscope image of millimetre-level cracks at SS304L/Ti6Al4V gradient structure, adapted from [31], (d) SEM images of IMCs found at the interface of Ti6Al4V/AA754, adapted from [26], (e) Microscope image showed the clear boundary formed at the interface of 316L/IN718, adapted from [29].

2.1.3 Multi-material Laser Induced Forward Transfer

LIFT is a precise additive manufacturing process that utilises the energy from a laser pulse to detach a donor film from an optically transparent carrier, which is then deposited onto a receiving substrate to build 3D structures layer by layer [7], [17]. LIFT is noted for its exceptionally high resolution, typically ranging between 0.1 to 10 μm, which makes it particularly suited for micro-scale 3D printing [7]. The process is versatile in terms of material compatibility, accommodating metals including Cu, Ag, V, Cr, Ti, Sn, W, Pd, Al, Au, Ni, and Pt [7], [40]. Both solid metals and liquid suspensions of metal particles can serve as the donor film in the LIFT process. As illustrated in Figure 2.14(a), the pulsed laser beam heats the interface between the carrier and the donor layer, facilitating the transfer of either a molten metal layer or a suspension of metal particles to the substrate. By changing the donor material, LIFT can rapidly

support multi-material manufacturing [7], [41], [42], [43], as depicted in Figure 2.14(b).

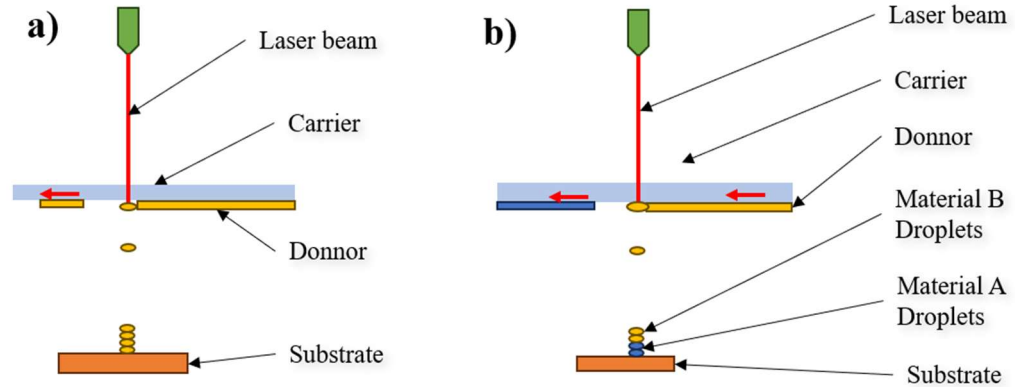


Figure 2.14 Diagrams of: (a) Single-material LIFT process, (b) Multi-material LIFT achieved by changing donor films.

LIFT's applications are predominantly on a micro scale, including the fabrication of micro energy storage components and microelectronic components [41]. Figure 2.15(a) outlines the SEM image production of a free-hanging spring structure [42], using gold (Au) film for the spring and copper (Cu) for the support. This structure is sequentially built with alternating layers of Au and Cu, as shown in Figure 2.15(b), and the support is later removed by etching in an FeCl_3 solution. Another notable application is the creation of a Pt-Au micro thermocouple [43], designed as a joint of two vertical intersected polylines as illustrated in Figure 2.15(c). Testing revealed that the voltage output of this thermocouple linearly corresponds to the temperature. Although LIFT has tried to produce some micro batteries and capacitors [7], [40], its small manufacturing scale and poor deposition repeatability limit further application.

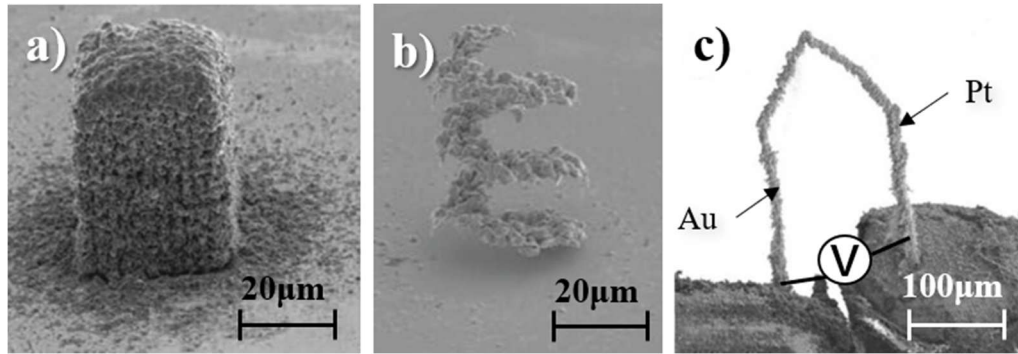


Figure 2.15 LIFT fabricated samples: (a) SEM images of Au spring with Cu support before etching, adapted from [42], (b) SEM images of the overhang Au spring, adapted from [42] and (c) SEM images of Au-Pt thermocouple, adapted from [43].

High porosity is a notable issue in LIFT, with porosity rates in some samples reaching up to 50% [7], [17]. Figure 2.16 (a) demonstrates a multi-material LIFT part with gaps and pores observed even from the surface. This is largely due to uneven droplet generation, which leaves gaps that are challenging to fill during subsequent deposition. Additionally, droplet splashing can exacerbate the creation of these pores. Furthermore, inadequate bonding at the joint is another critical problem [42]. This issue arises from both the presence of voids at the interface and the insufficient energy input during deposition. In this case, the subsequently deposited Cu particles lack the thermal energy required to remelt the previously deposited Au layer, resulting in a distinct boundary line at the interface, visible in Figure 2.16 (b). In certain applications where Cu acts merely as a soluble support material [42], [43], insufficient energy at the interface does not adversely affect the function. However, in cases requiring robust joints, such unmelted boundaries can substantially weaken the connection. Weak bonding at the joints, limited fabrication scale and unstable deposition are three main factors that hinder multi-material LIFT from becoming more useful.

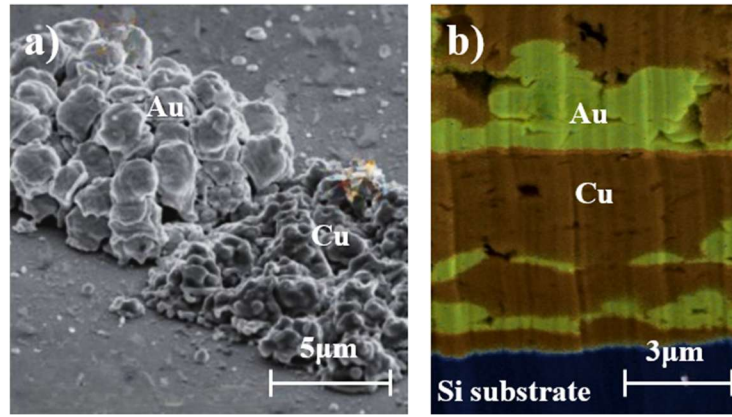


Figure 2.16 (a) SEM image of Au and Cu printings by LIFT, (b) SEM (left) and Energy dispersive X-ray (EDX) (right) images of un-melted boundaries and pores at the Au/Cu interface [42].

2.2 Molten Metal Jetting systems

The development of the MMJ technique has been driven by the expanding needs of the electronics industry, particularly for solder printing [44]. This technology has quickly evolved to enable the fabrication of free-form metal parts using materials with higher melting points [45], [46]. This subsection reviews advancements in MMJ systems, focusing on their methods for droplet generation.

MMJ technology primarily encompasses two approaches: Continuous Jetting (CJ) and Drop-on-Demand (DoD) [47]. The fundamental distinction between these methods lies in the delivery of molten metal from the nozzle: CJ produces a continuous stream of metal, which may break into droplets, whereas DoD ejects metal in the form of individual droplets, as depicted in Figure 2.17. In CJ, it is not possible to control each droplet individually, unlike the pixel-wise precision offered by DoD methods. Although early MMJ systems were limited to continuous jetting due to the actuator's operational frequency limitations [48], [49], [50], advancements in hardware have led to the development of high-frequency actuators and more sophisticated control modules. These improvements have established DoD as the predominant method in modern MMJ applications.

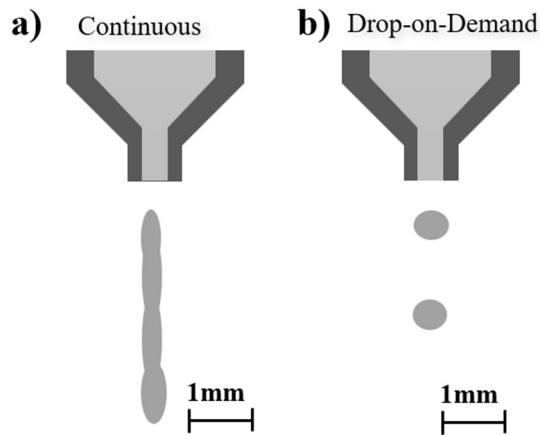


Figure 2.17 Diagrams of the continuous and DoD jetting method in MMJ

The actuation method is a critical feature in Molten Metal Jetting (MMJ) systems, dictating how molten metals are ejected. This section will explore four primary actuation methods used in MMJ: piezoelectric, pneumatic and magnetohydrodynamic (MHD). Each method's mechanism and example system setups will be discussed, highlighting their strengths and limitations and how these influence the performance and functionality of the systems.

Piezoelectric actuation MMJ

Piezoelectric actuation, widely utilised in inkjet technology, was one of the earliest methods adapted for MMJ systems [51]. Piezoelectric droplet generators in MMJ transfer the movement of a piezo crystal into an impact on molten metal, producing a jet at the orifice. These generators are generally categorised into two designs: squeeze mode and push mode.

An early-stage design of squeeze mode droplet generator aimed to jet solders with very low melting points, featured a horizontally aligned printhead as shown in Figure 2.18(a). Molten metal was stored in a glass tube positioned between two piezo crystals. Upon activation, the piezo crystals compressed the tube, ejecting molten metal. Indium alloy Inda-158, with a melting point of 70°C, was used, achieving minimum droplet sizes of 60µm at a maximum frequency of 500Hz [52]. Rumschoettel et al. later improved this design by positioning the piezo crystal at the base of a vertical printhead, as shown in Figure 2.18(b), allowing for the ejection of higher melting point Sn63Pb37 solder (melting point 183°C) [53]. Both configurations place relatively low demands on the

load-bearing and precision capabilities of the piezoelectric crystal. This makes squeeze-mode droplet generators well-suited for low-cost systems. However, this advantage comes at the expense of performance: the nozzle's maximum operating frequency is limited by the compression–recovery rate of the cartridge or container, which is usually significantly lower than the inherent frequency capacity of the piezoelectric crystal. The compression–recovery rate of the glass tube also increases the system response delay.

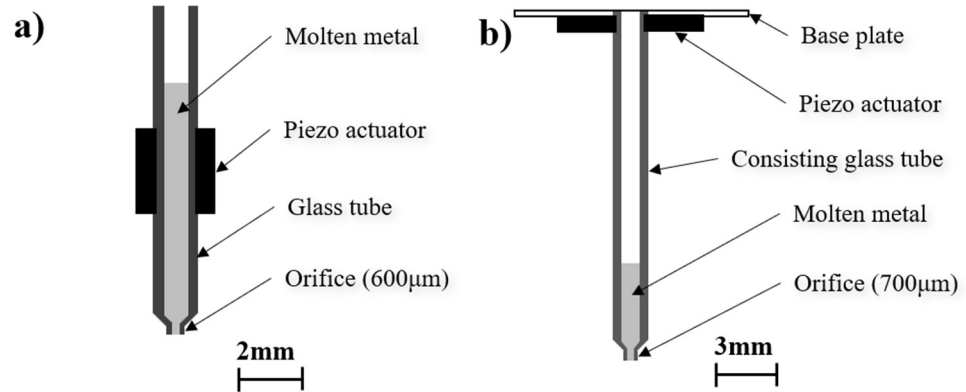


Figure 2.18 Diagrams of two piezoelectric droplet generator designs: (a) Earliest MMJ droplet generator designed by Marusak, (b) Improved design by Rumschoettel et al.

Push-mode droplet generator uses a piezo crystal directly vibrated to eject material [54], as depicted in Figure 2.19(a). Yamaguchi et al. demonstrated an MMJ printing with a push-mode generator using fusible alloy with a melting point of 47°C and achieved a stable jet of 200µm in diameter droplets. Jiang et al. followed with a similar mechanism, making full use of the frequency advantage of the piezo crystal and achieved a jetting frequency of 2800Hz in generating Sn-Pb solder droplets at high consistency [55]. Orme et al. designed a generator using a vibration rod to isolate the piezo from the molten metals, capable of handling materials like solder [50], [56] and aluminium [57], which have melting points as high as 660°C, as shown in Figure 2.19(b). Luo et al. further evolved this concept by replacing the piezo with an impact rod driven by a rotating cam, though this reduced the jetting frequency to a maximum of 25Hz and allowed the system to withstand temperatures up to 1200°C [58]. Yokayama et al. developed a design protecting the piezo material with a moveable diaphragm to separate it from the molten metal, effectively printing

Sn–3Ag–0.5Cu solder with a melting point of 220°C, as illustrated in Figure 2.19(c) [59]. Similarly, Lee et al. used this design to print Sn63Pb37 solder [60]. Though push-mode configurations achieved higher maximum working frequency than the squeeze mode ones, they showed higher demand on the piezo crystal's loading and thermal isolation.

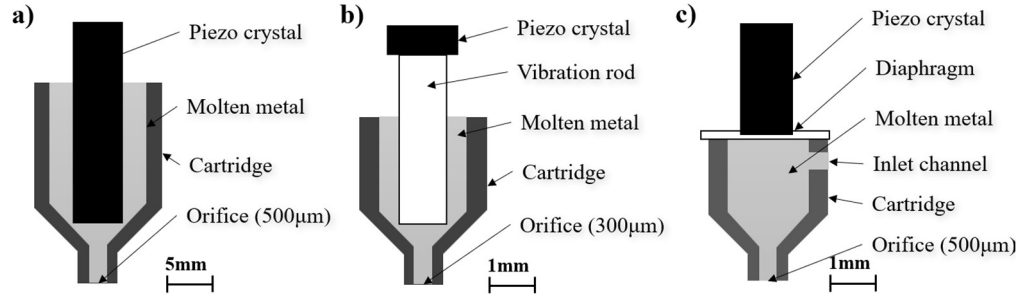


Figure 2.19 Diagrams of three push-mode piezoelectric actuators: (a) Piezo material in molten metal, (b) Vibration rod placed into the molten metal, (c) Molten metal separated by a close chamber.

A tough challenge for all the piezoelectric systems is that the working temperature is limited by the Curie temperature of piezo materials, which typically range between 150°C and 300°C, necessitating careful thermal isolation methods [50], [56], [57]. However, they are cost-effective due to the affordability of piezo actuators and controllers [54], [59]. Another significant advantage of piezoelectric systems is their ability to eject semi-conductive materials, as the ejection mechanism is based on mechanical impact only.

Pneumatic actuation MMJ

Pneumatic actuation in MMJ systems employs pressurised gas to eject molten metal droplets. A typical pneumatic MMJ system works as the diagram in Figure 2.20(a) [61]. Cao et al. [61] succeeded in printing Aluminium (Al) droplets with this setup and got a 700 µm diameter droplet using the nozzle at the orifice diameter of 300 µm.

A problem of pneumatic droplet generation is that the droplet size is always larger than the nozzle orifice, making it difficult to get smaller droplets. To reduce the problem, enhancing the wettability of the orifice was proven to be a solution. Based on this, Cheng et al. enhanced the pneumatic method by applying an aluminium oxide coating to the droplet generator's nozzle,

facilitating the jetting of indium, tin, lead, and zinc droplets with sizes ranging from 170 to 600 μm [62]. Another approach was proposed with the solution of the StarJet system [63], named after its unique nozzle orifice design surrounded by gas-supply channels, as depicted in Figure 2.20(b). This design, inspired by star tube toys to minimise bubble resistance, increases the wettability of the nozzle. Protective gas around the nozzle to prevent oxidation. The system achieved both continuous and DoD jetting by varying the gas pulse's shape and magnitude, successfully printing solder parts [64]. Further innovations by Lass et al. focused on refining the star-shaped nozzle to enhance performance, achieving a reduced droplet diameter of 60 μm and a maximum jetting frequency of 11kHz [65]. This modification improved the stability of droplet generation, contributing significantly to the system's efficiency.

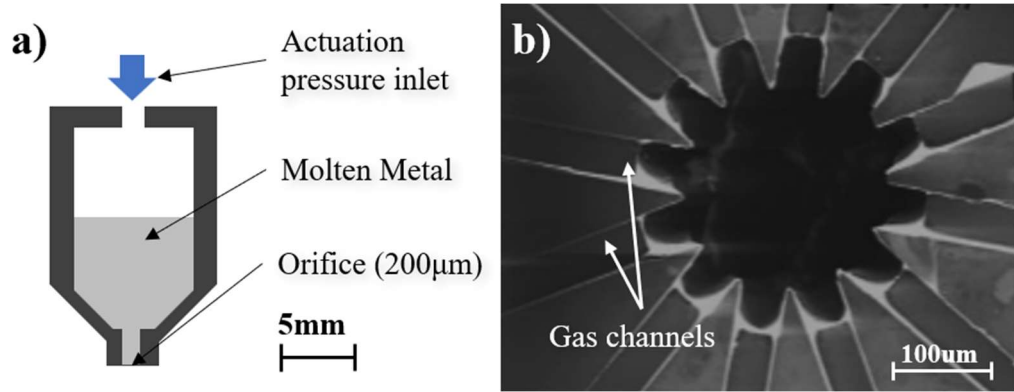


Figure 2.20 Schematic of: (a) The earliest pneumatic MMJ nozzle, (b) SEM image of StarJet nozzle orifice with gas channels, adapted from [63].

The evolution of pneumatic MMJ systems has primarily addressed the challenges associated with maintaining high jetting temperatures. A critical issue has been the thermal stability of the system's seals [66], necessitating advancements in sealing materials and cooling systems. Nozzle material selection is also vital to ensure compatibility with the molten metals and prevent reactions. For instance, Zhong et al. successfully melted copper at 1200°C and jetted Cu droplets using a pneumatic system with a graphite cartridge and seals capable of withstanding high temperatures [67]. The setup was enclosed in a glovebox to prevent oxidation at elevated temperatures. Although Cu droplets were produced, no 3D parts were successfully printed in this experiment. Moqadam et al. pushed the boundaries further by jetting steel droplets at

temperatures up to 1600°C [68]. Their system featured a well-designed cooling system to protect the valve from accumulated heat, allowing for the consistent generation of droplets at the desired diameter, which were then collected in quenching oil. However, similar to previous efforts, no 3D parts were printed using steel in this study. This limitation may be attributed to two main factors: the lack of a compatible substrate material and inadequate inter-droplet bonding.

Pneumatic systems face challenges with chamber sealing, which must endure significant temperature fluctuations, demanding high-quality sealing materials [47]. The droplet size tends to be several times larger than the nozzle orifice, limiting the achievable resolution [61], [69]. Despite these drawbacks, pneumatic systems can achieve high production rates and are capable of processing high-melting-point metals [61]. This method also benefits from the low system response delay in chamber pressure, which allows the droplet separation to be fast and sensitive, enabling the high-frequency DoD printing. Furthermore, pneumatic MMJ systems have no restrictions on the electric conductivity of materials, thus semi-conductive or non-conductive materials (for example, salt [70], [71]) can be printed.

Magnetohydrodynamic (MHD) droplet actuation

MHD-actuated MMJ is the first and only commercialised type of MMJ system. The system, initially developed by Vader et al. and named the Vader System, was later acquired by Xerox in 2021 and renamed ElemX. Further acquisitions led to its present iteration under ADDiTEC as ADDiTEC ElemX [72]. The core mechanism across all versions involves feeding aluminium wire into a ceramic heating chamber, surrounded by a coil that generates a transient magnetic field through electrical pulses. This field induces a circulating electric current in the liquid metal, creating a magnetohydrodynamic Lorentz force that propels the metal out of the nozzle [73], as demonstrated in Figure 2.21(a). The force F can be described by the equation:

$$F = J \times B \quad (2.1)$$

where J is the circulating current density and B is the time-varying magnetic flux density.

Sukhotskiy et al. conducted extensive modelling and experimentation on the Vader system, optimising parameters that led to successful aluminium part printing [74], [75]. The system's design includes argon as a protective gas to prevent oxidation at the nozzle and uses a computer to synchronise stage movement, wire feeding, and current changes, as shown in Figure 2.21 (b) to (d). The system's practical design facilitates easy installation of feedstock wire, enhancing user-friendliness.

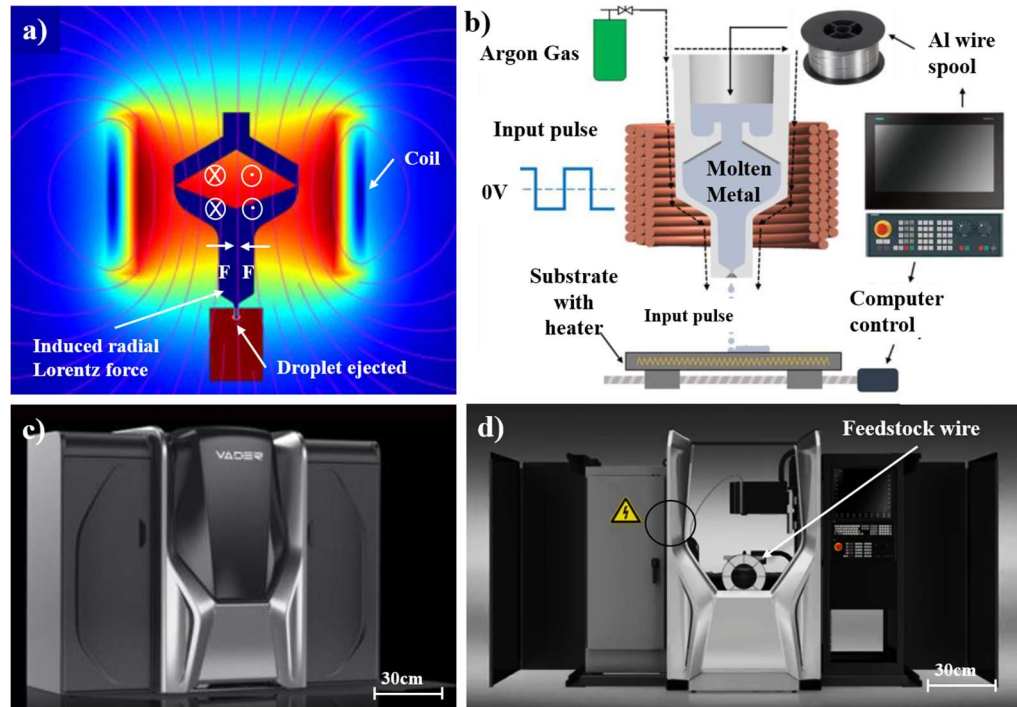


Figure 2.21 (a) Diagram of the Vader system printhead, adapted from [74] (b) System diagram of the Vader system, adapted from [74] (c) 3D model rendering of the Vader system, adapted from [74] (d) Feedstock wire in the explosion view of the Vader system, adapted from [74].

Another significant MHD-based MMJ system is the MetalJet [76]. In this setup, the nozzle is positioned between two permanent magnets, and the feedstock material is heated by induction. Electrodes near the orifice make contact with the molten metal, and a current pulse through these electrodes generates the Lorentz force required for ejection, as depicted in Figure 2.22 [76]. The MetalJet system achieves high precision with droplet sizes as small as $50\mu\text{m}$ and a high printing frequency up to 2000Hz , making it a highly competitive technology [45], [46]. Components like a graphite cartridge capable of withstanding

temperatures above 2000°C allow the printing of materials with high melting points, such as silver and copper [45], [77].

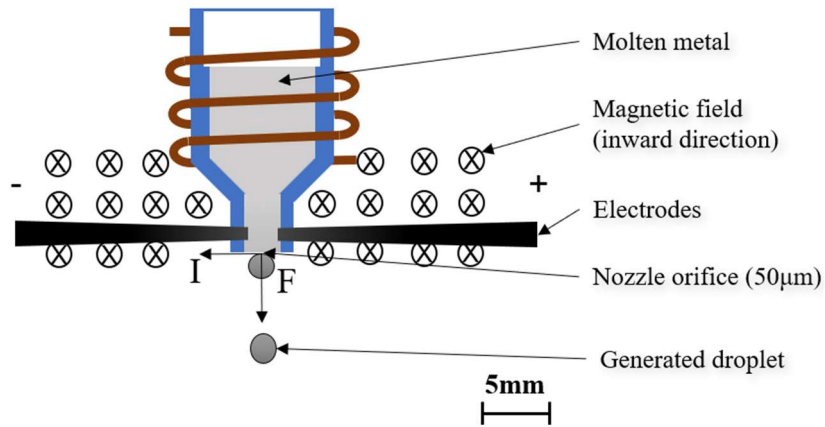


Figure 2.22 Diagrams of the MetalJet printhead showing the printhead, electrodes and magnetic field.

Though the MHD method shows a high demand on the equipment, Luo et al. still managed to design a more accessible, desktop-level MHD MMJ system [78]. This simplified setup successfully deposited solder bumps on PCB boards at the price of lower resolution at 500µm. The lack of protective gas also restricted its use primarily for soldering. Despite all the shortcomings, this research still provides the possibility of making MHD setups smaller in size and more affordable in cost.

Above all, MHD systems showed the obvious advantage of high temperature capability. The system's maximum operating temperature is high, as it is mostly determined by the materials of cartridges, coatings, and electrodes, rather than by sealing materials or actuators [45], [72]. MHD systems can achieve high production rates and high-frequency DoD printing due to their current-based actuation mechanism. The maximum resolution is typically around the size of the nozzle orifice. However, MHD systems usually require materials with high electrical conductivity for effective operation, which to some extent, limits their material choice.

2.3 Molten Metal Jetting process study

This section explores the recent advances in MMJ process study, organised around key areas of droplet generation, droplet deposition, materials development and applications. These segments provide a comprehensive understanding of the various aspects of MMJ research and technological progress.

2.3.1 Droplet generation

At the early stage of MMJ development, droplet generation parameters such as voltage and pulse shape have evolved from the understanding of Inkjet [50], [54], [79]. Similar to the analysis of polymer, Weber number (We) and Ohnesorge number (Oh) are used to analyse the dynamics of molten metal. These parameters are crucial for understanding the behaviour of the molten metal and the underlying mechanisms that influence jet stability and droplet separation. The Weber number represents the ratio of inertial forces to surface tension forces, which is defined as:

$$We = \frac{\rho v^2 L}{\sigma} \quad (2.2)$$

where ρ is the density of molten metal, v is the speed of the jet by droplet, L is the diameter of metal ejected and σ is the surface tension of molten metal. A Weber number greater than one ($We > 1$) suggests that the dynamics are driven by inertial forces ("impact-driven"). Conversely, a Weber number less than one ($We < 1$) indicates a dominance of surface tension forces ("capillary-driven").

The Ohnesorge number (Oh) represents the ratio of viscous forces to the combined effects of inertial and surface tension forces, defined as:

$$Oh = \frac{\mu}{\sqrt{\rho \sigma L}} \quad (2.3)$$

Where μ is the dynamic viscosity. An Oh number greater than one ($Oh > 1$) means viscous forces prevail, potentially inhibiting jet breakups and favouring the formation of a continuous jet. An Oh number less than one ($Oh < 1$) indicates

that inertial and surface tension forces are more influential. The ideal range for inkjet printing, ensuring a balance between droplet formation and jet stability, is $0.1 < Oh < 1$ [79].

Given that molten metals exhibit higher viscosity, surface tension, and density than typical inkjet materials, the principles of droplet generation in inkjet cannot be directly transferred to MMJ without adjustments. The specific ejection and breakup mechanisms unique to MMJ are essential for optimising the process. Luo et al. developed a 2D axisymmetric model to describe droplet formation. In his case, Weber numbers ranged between 0.02 to 0.46 and Oh numbers between 0.0012 to 0.0018. The model identified that droplet separation is predominantly influenced by capillary disturbances caused by surface tension [80]. Based on a similar method, Beck et al. used a Volume of Fluid (VoF) numerical model to explore MMJ droplet generations with a wide range of Weber numbers and successfully predicted the metal droplet extrusion and breakup processes [81]. Compared to the model built by Luo et al., this model demonstrated broader applicability, as it could describe droplet formation dynamics across a wider range of Weber and Ohnesorge numbers.

In all three actuation methods, droplet formation in MMJ involves an interplay of four key forces: pulse pressure, inertial force, surface tension, and viscous force. Initially, molten metal is retained within the nozzle by surface tension, as shown in Figure 2.23(a). When a positive pressure pulse is applied, the molten metal protrudes from the nozzle orifice driven by actuation pressure, as shown in Figure 2.23(b). As the pressure subsides, a retraction force acts on the metal near the orifice, and with the effect of inertia, a "bridge" forms between the nozzle and the extending molten metal as shown in Figure 2.23(c). This bridge eventually breaks when the outward portion of metal forms a sphere, completing the droplet formation Figure 2.23(d). In this stage, surface tension is the driving force for separation as the extruded metal tends to minimise its surface energy [81], [82].

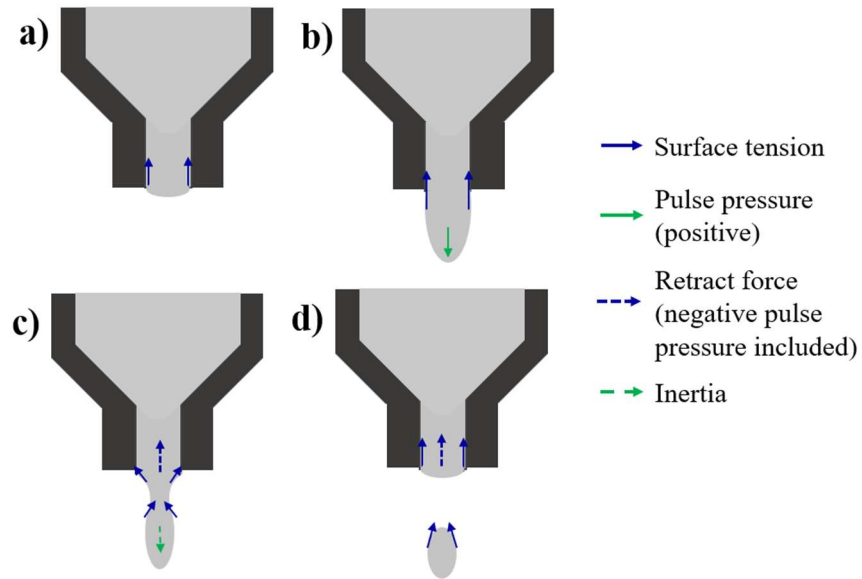


Figure 2.23 Diagram of the four stages of droplet formation in MMJ: (a) Molten metal stored in the nozzle, molten metal is held by surface tension, (b) Molten metal is pushed out by pulse pressure, (c) A “bridge” formed by inertia as positive pulse pressure disappears, (d) Surface tension drives the separation and a droplet is formed.

Droplet formation in molten metal jetting is defined by the dynamics of the generation pulse, including pulse pressure, width, shape, and dwell time, as demonstrated in Figure 2.24(a). Understanding how these parameters influence droplet size, velocity, and stability is critical to improving jetting reliability and frequency. Pulse pressure and width were usually adjusted as a parameter pair, as their combination affects the volume, speed and breakup force of the ejected molten metal [59], [83], [84]. Yokoyama et al. [56] achieved a higher jetting frequency by using a narrower pulse width but pointed out that pulse magnitude needs to be increased accordingly. The droplet velocity was found to correlate with the pulse pressure. These findings are verified by several other studies [83], [84]. Using the numerical model previously developed by Luo et al. [80], Zhong et al. [84] further noticed that the magnitude (pulse pressure) has a limit; if exceeded, satellite droplets will be formed. This means that the minimum pulse width according to the maximum magnitude threshold hindered the jetting frequency from becoming infinite.

Besides speed and frequency, the size of the droplets can be influenced by the parameter pair of dwell time and magnitude, as reported by Shokraneh et al. [85]

introduced pulse shape and dwell time in droplet formation study. Comparing sinusoidal and square waveforms, with and without dwell times, they showed that both higher peak values and longer dwell periods enlarge droplet size.

Lin et al. [82] incorporated the role of negative pulse pressure in their studies, providing a comprehensive view of how both positive and negative pulses influence droplet behaviour. A diagram illustrating the generation pulse with negative pressure is shown in Figure 2.24(b). The findings suggest that the suction effect of the negative pulse aids in droplet detachment by pulling back the melt tail, thus reducing satellite formation.

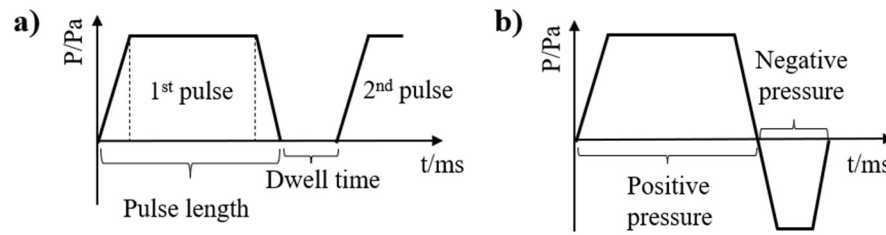


Figure 2.24 Example of MMJ actuation pulses: (a) A pulse with only positive pressure, (b) A pulse with negative pressure.

Beyond internal pulse modulation, recent research has explored external or secondary waveforms to improve droplet separation and suppress satellite formation in molten metal jetting. Secondary waveforms are harmonics superimposed on the primary waveform. These waveforms share the frequency of the main waveform but have significantly smaller amplitudes. Secondary waveform can help with the separation stage of the jetting. For example, Amirzadeh et al. [86] introduced a secondary gas flow technique that delivers a controlled jet of gas around the nozzle during droplet formation. This auxiliary flow applies an additional mechanical force during the critical separation phase, promoting easier detachment, as shown in Figure 2.25 (a). The resulting pneumatic assistance reduced droplet diameter by approximately 15%, likely due to earlier and more stable pinch-off driven by the outward gas momentum. Another case is that the odd harmonic superposition perturbations can be used to refine the main for reducing satellites, which is applied by Lyu et al. [87]. The waveform applied was depicted in Figure 2.25 (b). Their parameter study

showed that the number of harmonics and their phase relationships significantly influence droplet size and velocity, offering a tunable strategy for droplet control.

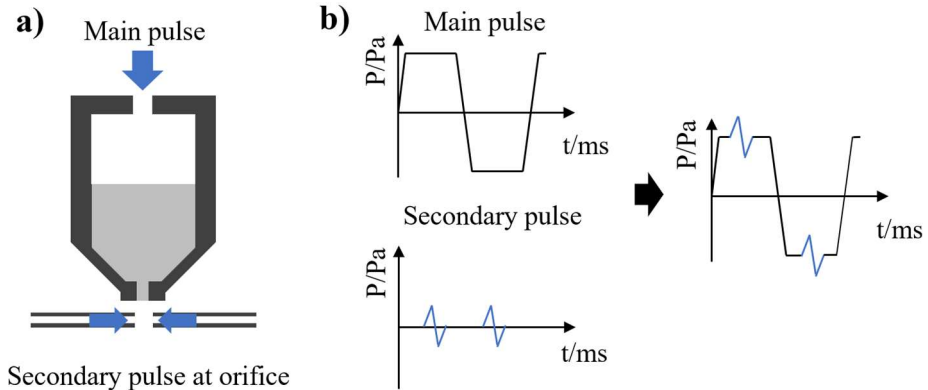


Figure 2.25 (a) Diagram of the pneumatic setup with secondary pulse applied at orifice (b) Diagram of main pulse, secondary pulse and their combination.

Traditionally, MMJ droplet generation and ejection have been observed using stroboscopic or high-speed cameras. However, Wang et al. [88] advanced the dynamic monitoring of this process by substituting these cameras with a microwave transmitter and receiver. Notably, the microwave monitoring data, presented as a one-dimensional matrix, processes faster than image data, which is a 2D array. This speed gives space to the integration of machine learning (ML) into in-situ process control [89]. In their study, variables such as droplet volume, velocity, and satellite presence, captured through one-dimensional waveforms, are processed through a multi-layer neural network. The output then dynamically adjusts the injection voltage that controls the jetting, successfully stabilising the jetting process.

Building on this approach, Gaikwad et al. [90] further predicted droplet shape and velocity based on the microwave input using an improved ML model. Unlike Wang et al. [89], this study did not require pre-analysis of the waveform signal; instead, it was compacted into a one-dimensional array and directly input into the neural network. This method enables the prediction of droplet characteristics before deposition, laying the groundwork for flaw prediction in the printing process.

Besides droplet generation, Rehekampff et al. [91] introduced an in-situ method to evaluate the surface quality during the printing process. This method utilises

a standard optical camera to capture images of the printed part at different focal points. A sharp contour in the image indicates that the observed feature is in focus, enabling the creation of a detailed height map of the surface for further analysis. Though no closed-loop control is built due to the image processing time, this monitoring method provides possibilities for adding real-time AI closed-loop control in future.

2.3.2 Droplet deposition

2.3.2.1 Wetting and solidification mechanisms

In the MMJ deposition process, the droplet-substrate wetting determines whether the droplet will be held on the substrate under controlled deposition or rebound and leave the substrate. The wetting mechanism of liquid metal during MMJ deposition encompasses four distinct stages: kinematic, spreading, relaxation (or retraction), and equilibrium, as illustrated in Figure 2.26(a-d) [46], [92].

- **Kinematic Phase:** As the droplet impacts the surface, the contact area, termed the "contact line," begins to expand. This initial contact, as seen in Figure 2.26(a), is primarily shaped by the droplet's impact and inertia, with wetting playing a minimal role.
- **Spreading Phase:** The contact line extends further, creating a rim of lamella above it, as depicted in Figure 2.26(b). The extension continues until the surface forces counteract the spreading momentum, eventually halting the expansion. Wetting failed to play a role in the spreading phase, while the inertia of the droplet dominates [92].
- **Relaxation Phase:** After reaching its maximum spread, the droplet begins to retract, reducing the contact angle and pulling the contact line inward, as shown in Figure 2.26(c). This phase is crucial as the wettability of the substrate influences whether the droplet will rebound or stabilise on the surface.
- **Equilibrium Phase:** The droplet's oscillations diminish and cease altogether, with the contact line settling at an equilibrium state shown in

Figure 2.26(d). This final stage stabilises the droplet, finalising its position and form on the substrate.

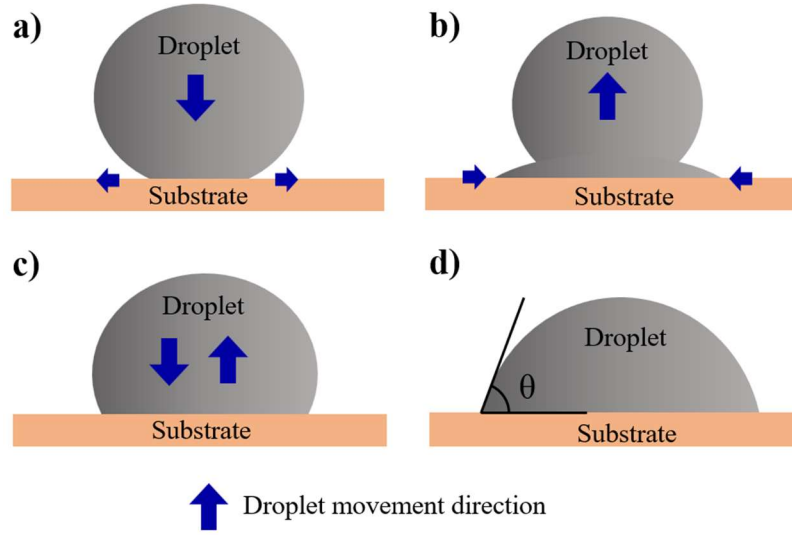


Figure 2.26 Four phases in MMJ droplet solidification: (a) Kinematic phase, (b) Spreading phase, (c) Relaxation phase, (d) Equilibrium phase.

The final contact angle and spreading behaviour of the metal droplet largely depend on the type of droplet-substrate wetting: reactive wetting or non-reactive wetting. [93].

Non-reactive Wetting

This occurs when a liquid metal droplet spreads on a solid substrate without undergoing any chemical reactions or interfacial dissolution between the two materials[94]. Illustrated in Figure 2.27, non-reactive wetting is determined by the balance of surface energies that define the contact angle θ . The intrinsic contact angle θ_Y in this case is given by the classical Young's Equation:

$$\cos \theta_Y = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} \quad (2.4)$$

where the quantities σ_{SV} and σ_{LV} define the surface energy of the solid and liquid, respectively, and σ_{SL} the solid-liquid interface energy.

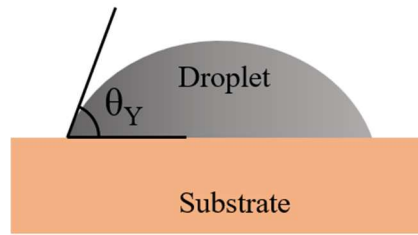


Figure 2.27 Diagram of non-reactive wetting model

Reactive Wetting

This type of wetting involves a chemical reaction at the droplet-substrate interface, often resulting in the formation of new compounds or interfacial phases [95], [96]. It is characterised by substrate dissolution into the liquid, interdiffusion of elements, or the formation of intermetallic compounds (IMCs). Reactive wetting can be further divided into three models [96], [97]:

- **Reaction Product Control (RPC) Model:** In this model, wetting is predominantly influenced by chemical reactions at the interface. As shown in Figure 2.28, the contact angle, θ , is altered by the formation of IMCs at the interface [98], [99].

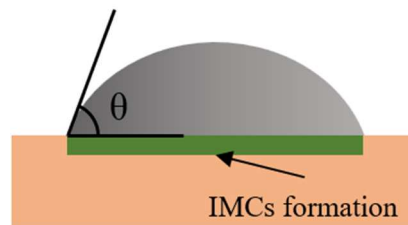


Figure 2.28 Diagram of reactive wetting model with IMCs formed at droplet-substrate interface (RPC model)

- **Dissolutive Wetting Model:** Governed by the diffusion of atoms across the droplet-substrate interface, this model is illustrated in Figure 2.29 [100], [101]. The diffusion between the substrate and the liquid metal results in a contact angle θ_2 below the substrate boundary. The dynamics of wetting depend on the diffusion of metal atoms, which is highly sensitive to temperature changes.

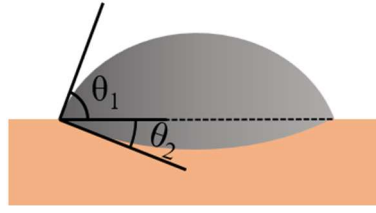


Figure 2.29 Diagram of dissolutive wetting model. θ_1 represents the contact angle above the substrate, while θ_2 represents the contact angle below the substrate.

- **Dissolutive Wetting with Reaction Product:** This model involves both interdiffusion and the formation of IMCs, integrating the mechanisms of the RPC model dissolutive wetting model, as shown in Figure 2.30 [93], [97].

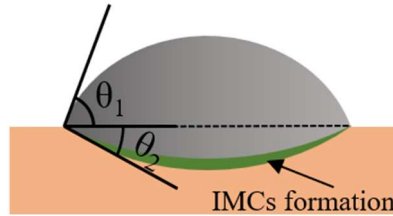


Figure 2.30 Diagrams of a combination of RPC model and dissolutive wetting model.

The droplet deposition in MMJ transcends the mere equilibrium state of wetting. Due to continuous heat dissipation, the droplet begins solidifying before reaching the equilibrium contact angle. Two key indicators, solidification angle and spreading factor, were used to describe droplet morphology. The solidification angle refers to the contact angle at which the droplet solidifies, while the spreading factor is the ratio of the diameter of the solidified droplet to that of the liquid metal. The ideal final solidification morphology of a droplet should have a solidification angle smaller than 90° , but should also avoid droplet over-spreading, which will decrease the maximum resolution in the printing.

The substrate temperature and nozzle temperature form a critical parameter pair that governs contact angle evolution, spreading diameter, and solidification angle, as reported by Gilani et al. [46]. Sn was printed to the Cu substrate at various substrate temperatures and nozzle temperatures. The findings,

illustrated in Figure 2.31 (a) to (c), demonstrated that as nozzle temperature decreases, the solidification angle increases. This occurs because lower droplet temperatures result in shorter cooling time upon impact, leading to the solidification before reaching the equilibrium state. Consequently, the contact line is fixed early, exhibiting a solidification angle increase from 80° to 110° . On the other hand, decreasing the substrate temperature brings shorter solidification time, which initially raises the solidification angle and then reduces it, as shown in Figure 2.31 (d) to (f) [46]. Typically, the spreading factor increases with substrate temperature, but the special case is attributed to the reactive wetting on the Sn-Cu interface, which affected the wetting angle. In the meantime, substrate material also makes a difference by influencing the wettability and heat transfer rates, which can impact the solidification dynamics [46]. Additionally, Zhou et al. [102] reported that environmental oxygen could suppress droplet spreading by oxidising the liquid metal's surface, which can be regarded as an external factor.

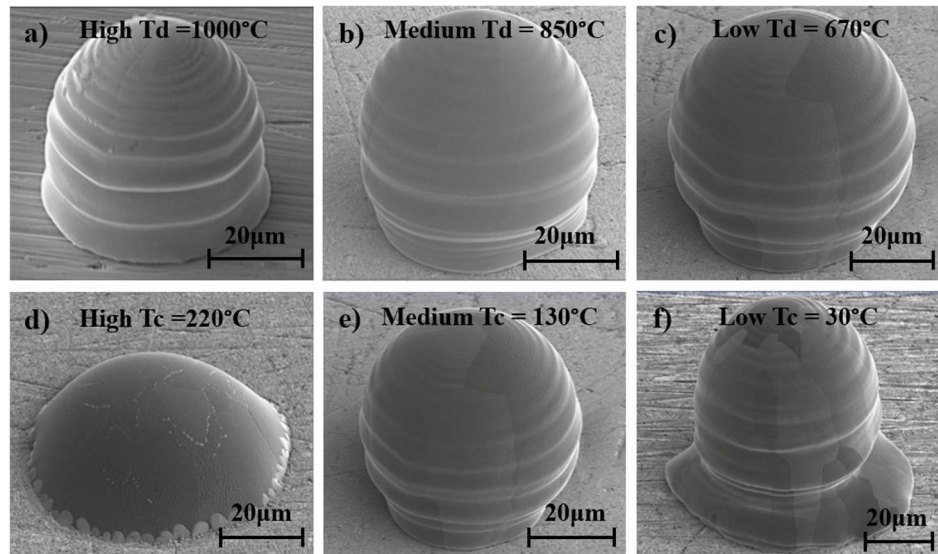


Figure 2.31 (a)-(c) SEM images of Sn droplet deposit on 50°C Cu substrate at nozzle temperature of 1000°C , 850°C and 670°C . (d)-(f) SEM images of Sn droplet deposit on Cu substrate at substrate temperatures of 220°C , 130°C and 30°C , the nozzle temperature is 850°C . Images adapted from [46].

It can be concluded from this research that the optimal droplet spacing (ds_{opt}) will change as substrate temperature, nozzle temperature or substrate

temperature changes due to the change in spreading factor. This has been verified by several studies [103], [102].

Improper settings of the droplet temperature and substrate temperature parameter pair can also bring droplet height variations. These variations were found to be caused by droplets solidified while oscillating during the relaxation stage [104]. Increasing the substrate or nozzle temperature can help reduce this problem by allowing longer solidification time. Li, et al. [105] noted that droplet height could vary based on substrate, influenced by differences in thermal conductivity, which will finally affect solidification times.

In most MMJ applications, high Weber numbers are usually avoided to reduce droplet splash or form an irregular shape. The research mentioned above was all conducted in low We number ($We < 1$ or $We \approx 1$). A counterexample is reported by Wang et al. [106], who observed that large We values led to excessive spreading or even splashing of droplets. The study showed that overly flat droplets formed due to the significant impact force during the kinematic phase, as depicted in Figure 2.32(a). Such droplets often exhibit irregular rims and solidify prematurely, presenting challenges in building accurate 3D structures, as seen from the top view in Figure 2.32(b).

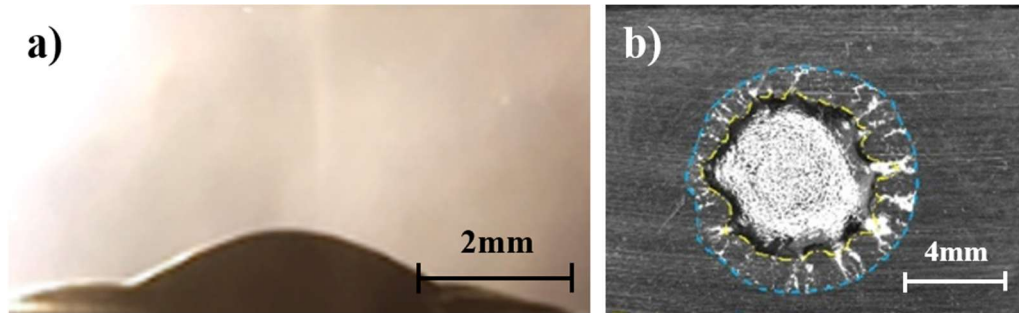


Figure 2.32 (a) Camera image with side view of over-spread droplet printed at high We number (b) Microscope image of an MMJ droplet with irregular rim.
Adapted from [106]

Besides droplet morphology at solidification, achieving robust droplet-substrate bonding during the solidification process is also fundamental in MMJ printing, as inadequate bonding can lead to defects such as droplet displacement or delamination. This bonding is essential to the deposition behaviour of droplets

on various substrates. Three primary types of droplet-substrate bonding have been identified:

- **Physical adsorption (Van der Waals force):** This represents the weakest form of bonding, where the droplet loosely attaches to the substrate. Typically observed at the interface of the MMJ Al droplet on the gypsum substrate [107] and Cu droplet printed on AlN/Al₂O₃ substrate [77]. Yi, et al [107] noted issues such as droplet rebound when depositing molten Al onto gypsum substrates, attributing this to poor wetting and weak Van der Waals forces.
- **Metallic Bonding:** This type of bonding occurs when similar metals come into contact, such as Cu on Cu or Sn on Sn substrates [46], [77]. The strength of this bond depends significantly on the extent of remelting at the interface. The concept of interface temperature indicates the temperature at the droplet-substrate contact line. In dual-metal printing, effective metallic bonding can be achieved when the temperature of the interface is maintained at a high level, allowing remelting and the formation of a robust metallic bond. This bonding is particularly temperature-sensitive and can be strengthened by increasing the substrate temperature (T_s) or the droplet temperature (T_d).
- **Diffusion Bonding:** This bonding mechanism relies on atomic interdiffusion and often involves the formation of intermetallic compounds (IMCs) at the interface, which typically occurs without remelting the substrate [97]. A representative example is the deposition of molten Sn droplets on a solid Cu substrate: although the energy of the Sn droplets is insufficient to remelt the Cu surface, a strong bond is still achieved through the formation of Cu–Sn IMCs such as Cu₆Sn₅ and Cu₃Sn, as shown in Figure 2.33 [46], [108]. Increasing substrate temperature has been shown to thicken the IMC layer, thereby strengthening the bond. Additionally, the application of an intermediate coating, such as a silver layer, on a gypsum substrate, has proven effective in promoting Al–Ag IMC formation, which improves bonding and mitigates issues like droplet rebound [107]

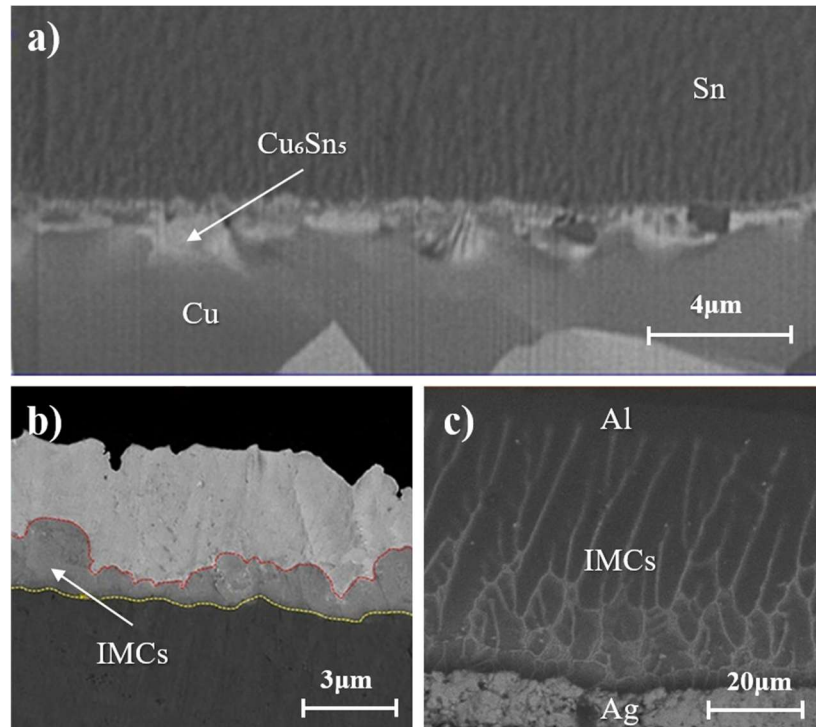


Figure 2.33 SEM images of droplet-substrate cross-section: (a) Cu₆Sn₅ formed at Cu-Sn interface, adapted from [46] (b) Cu-Sn IMC at the interface, adapted from [108] (c) Al-Ag IMC formed by Al droplets and Ag coating, adapted from [107].

The presence of argon protection gas entrapment during printing can lead to defects such as internal porosity and weakened bonding to the substrate, as demonstrated in Figure 2.34 by Yi et al. [109]. This issue is predominantly influenced by the wettability of the droplet. Droplets with a contact angle below 50° tend to allow gas bubbles to rise into the droplet, whereas a contact angle above 90° often results in the gas remaining trapped at the droplet's base. Modulating the droplet velocity has been identified as a method to reduce gas entrapment and enhance overall part quality.

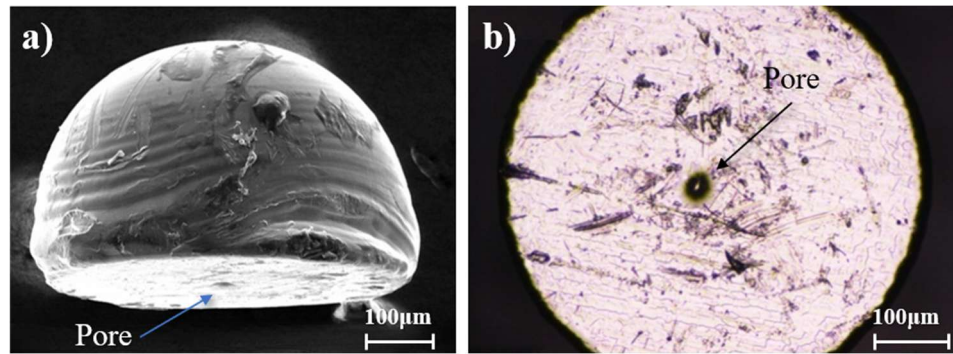


Figure 2.34 Diagrams and SEM image showing the entrapped gas hole: (a) side view and (b) bottom view.

2.3.2.2 Inter-droplet voids and bonding

Voids formed between deposited droplets in MMJ not only compromise the mechanical integrity of the printed structure but also degrade its electrical conductivity. Achieving strong inter-droplet bonding while minimising porosity is therefore essential for both structural and functional performance. Two primary mechanisms have been identified as major contributors to void formation: wetting failure induced by surface ripples and cold lap defects at the base of solidified droplets.

In several studies, ripples have been observed on the surface of solidified droplets [46], [110], [111]. These ripples, appearing as concentric circles on the droplet's outer surface, originate from the centre and are depicted in Figure 2.31 (a)-(c), (e) and (f), and Figure 2.35(a). The formation of ripples is attributed to the oscillations occurring during the droplet's relaxation phase, with the distance between the ripples generally decreasing from bottom to top. This pattern occurs because solidification progresses from the bottom upwards, and the oscillation period shortens as the temperature declines. Consequently, these ripples create regions that cannot be fully wetted by adjacent droplets, as demonstrated in Figure 2.35(b). The trapped ambient gas in the grooves prevents complete wetting due to the opposing forces of capillary pressure (P_c), which draws in the liquid metal, and gas pressure (P_g), which pushes it out, halting the filling process when P_g equals P_c . This type of porosity not only reduces the density of the part but also weakens inter-droplet bonding [110] and increases thermal resistance [46]. The mechanism of reducing or eliminating ripples is to extend

the droplet solidification time. Thus, this can sometimes be achieved by two main approaches: printing at substrate temperature above half of the melting point of droplet material, and printing on substrates with low thermal conductivity, as illustrated in Figure 2.31(d) and Figure 2.35(c) [46], [110].

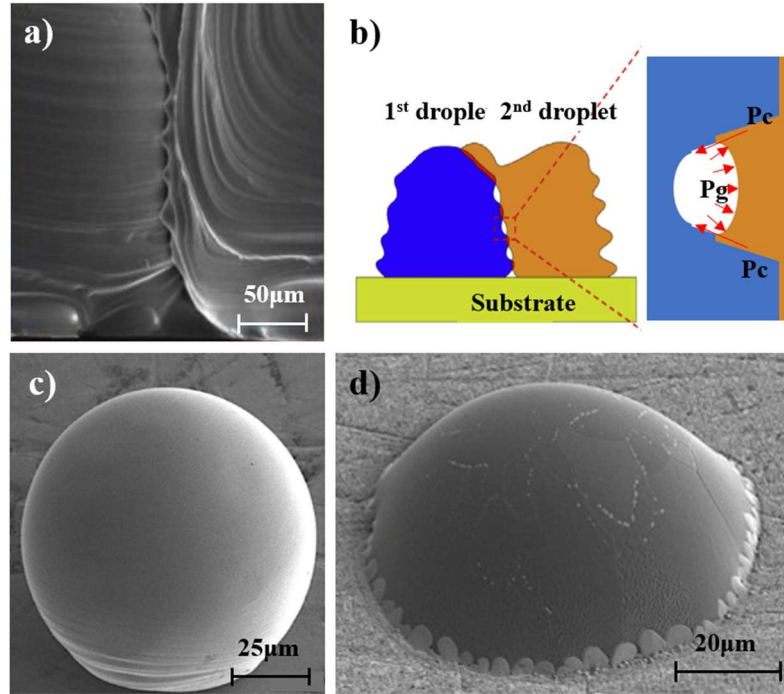


Figure 2.35 (a) SEM image showing the ripples at two neighbouring Al droplets printed at $T_s = 250^\circ\text{C}$ Al substrate, adapted from [110] (b) Diagram showing the unwetted regions at ripples of two MMJ Al droplets (c) SEM image showing a Sn droplet print on $T_s = 50^\circ\text{C}$ Zn substrate with no ripple, adapted from [46] (d) SEM image of a Sn droplet print on $T_s = 220^\circ\text{C}$ Cu substrate with no ripple, adapted from [46].

Research has also highlighted that pores can form at the junctions of adjacent droplets close to the substrate during the deposition process, as shown in Figure 2.36(a) [112]. Yi et al. [110] and Dou et al. [113] have explored the dynamics behind this phenomenon. During deposition, the droplet contacts both the substrate and another droplet almost simultaneously. Solidification commences from the contact lines and moves perpendicularly, often solidifying the metal before it can fill the corners formed by previously solidified droplets, thus creating a 'cold lap' between them. To mitigate this issue, adjustments are necessary either in the liquid metal's solidification time or in the angle of solidification relative to the previous droplet. These adjustments can be

managed by optimising the substrate temperature-droplet temperature (T_s-T_d) parameter pair or by using substrates with lower thermal conductivity. Furthermore, adjustments to droplet spacing (ds) are crucial, as highlighted by Dou et al. [114], who noted that spacing should be calibrated to balance both the solidification angle and droplet spreading to effectively eliminate cold laps at the droplet base. Su et al. [115] verified this approach, fine-tuning the optimal droplet spacing according to various T_s-T_d pairs, successfully creating aluminium traces without cold gaps, as shown in Figure 2.36(b). Similarly, Ploetz et al. [116] applied this method to deposit bronze material (CuSn8) with a smooth surface and minimal internal porosity, employing an appropriate T_s-T_d parameter pair. Li et al [111] ascribed the pore formation to the speed of the substrate in their study, but the parameter that actually worked was the droplet spacing (ds).

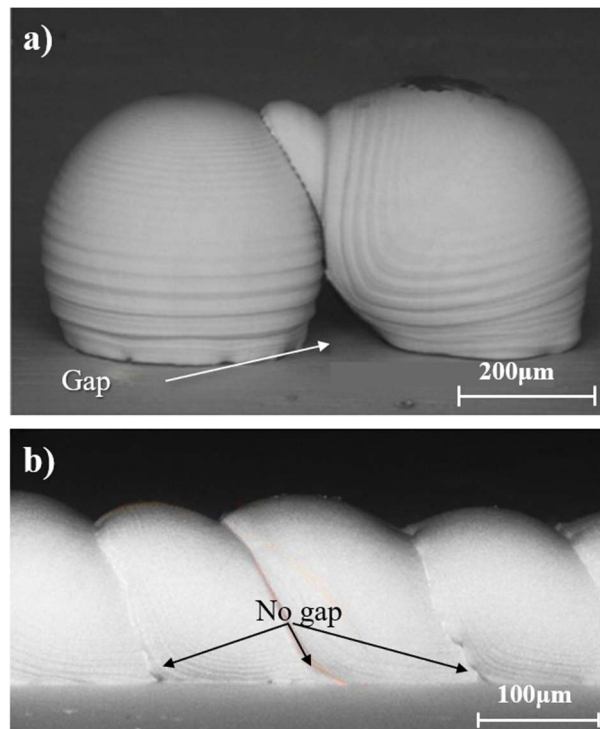


Figure 2.36 (a) SEM images of two Al droplets with bottom cold laps (b) SEM image of an Al trace printed without a gap at the bottom

In addition to void formation, weak inter-droplet bonding presents another critical challenge in MMJ. While voids compromise material continuity, insufficient metallurgical bonding can lead to poor load transfer across droplets,

thereby reducing the mechanical integrity of the printed part. This issue was first reported in aluminium-based MMJ processes, where distinct droplet boundaries were observed, as shown in Figure 2.37(a) [57]. Such boundaries indicate weak bonding and result in reduced mechanical strength, particularly problematic in structural applications [117].

To investigate the underlying causes of weak inter-droplet bonding in MMJ, a range of numerical modelling approaches has been explored. Himmel et al. [118] and Chao et al. [119] employed simplified 3D mesh-based models to simulate temperature distributions during sequential droplet deposition. In these models, each newly deposited droplet was abstracted as a high-temperature cube, and the deposition sequence was represented by the addition of successive cubes. While these models effectively captured general thermal dynamics in MMJ processes, they lacked the resolution to represent the detailed behaviour of individual droplets. To address this limitation, Li et al. [111] developed a more refined set of models simulating single droplets, pairs of adjacent droplets, and three successively deposited droplets. These models enabled more accurate predictions of temperature gradients across droplet interfaces. The results revealed that the temperature gradients were typically aligned parallel to the contact lines between droplets, indicating that solidification progressed vertically within the liquid phase of each droplet.

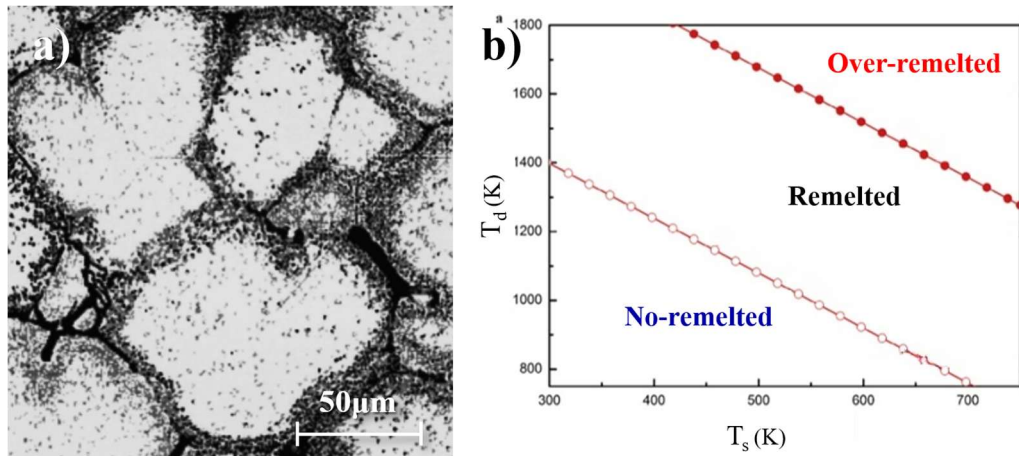


Figure 2.37 (a) SEM image showing clear boundaries and gaps between deposited Al droplets, adapted from [57] (b) 3 regions in the T_s - T_d map, divided by remelting of the interface, adapted from [111]

A key outcome from these studies is the identification of interface temperature as a critical factor influencing inter-droplet bonding. Local remelting was observed when the interface temperature exceeded the melting point of the droplet material, significantly enhancing metallurgical bonding at the interface [119]. Research has demonstrated that this temperature can be effectively controlled by adjusting both the nozzle temperature and the substrate temperature [111], [118], [119], [120]. These two parameters form a pair that divides the process space into three distinct regimes: no-remelt, remelt, and over-remelt, as depicted in Figure 2.37(b). Robust bonding is generally achieved within the remelt and over-remelt zones. However, in the over-remelt region, excessive remelting can cause the droplet to shift from its intended position before solidification, leading to geometrical inaccuracies in the printed part [117]. Notably, this parameter space does not account for the cumulative thermal effects arising from successive droplet deposition. Himmel et al. [121] addressed this gap by examining how consecutive droplets influence interface temperature. Their findings revealed that, in addition to the substrate and nozzle temperature pair, jetting frequency plays a vital role by contributing to thermal accumulation. This insight is particularly relevant for cases involving materials with low thermal conductivity, either in the substrate or the droplet, where heat dissipation is limited.

To assess the influences of interface temperature on the mechanical properties of printed parts, Himmel et al. [118] and Zuo, et al [117] conducted tensile tests on samples machined into tensile bars. Zuo et al. [117] discovered that interface remelting significantly enhances the tensile strength and elongation of the material. Complementing this Himmel et al. [118] found that the wetting behaviour of adjacent droplets is also influenced by interface temperature, with optimal tensile strength occurring in samples where the interface temperature was below the solidification temperature.

2.3.2.3 Heat accumulation

Heat accumulation is a notable defect observed during the continuous vertical deposition of molten metal droplets, where the diameter of the printed pillar tends to increase with the height and deposition frequency [122], as illustrated

in Figure 2.38(a). Liu et al [123] developed a VoF model to describe this phenomenon, which they divided into three stages of heat accumulation, depicted in Figure 2.38(b).

Stages of Heat Accumulation

- **Early Deposition Stage (Region I):** Initially, there is a significant temperature gradient and a short heat transfer path from the droplet to the substrate, facilitating rapid heat dissipation. In this phase, heat accumulation does not adversely affect the droplets, allowing for standard solidification and deposition behaviours as shown in Region I in Figure 2.38(b).
- **Middle Deposition Stage (Region II):** As the deposition progresses vertically, heat begins to accumulate due to the increasing stack of droplets, which extends the heat transfer path compared to the early deposition stage. This results in a longer solidification time, leading to more pronounced droplet spreading and enhanced inter-layer bonding. This stage is characterised by flatter droplet morphology and remelted boundaries, where the effects of heat accumulation are generally beneficial, as shown in Figure 2.38(b), region II.

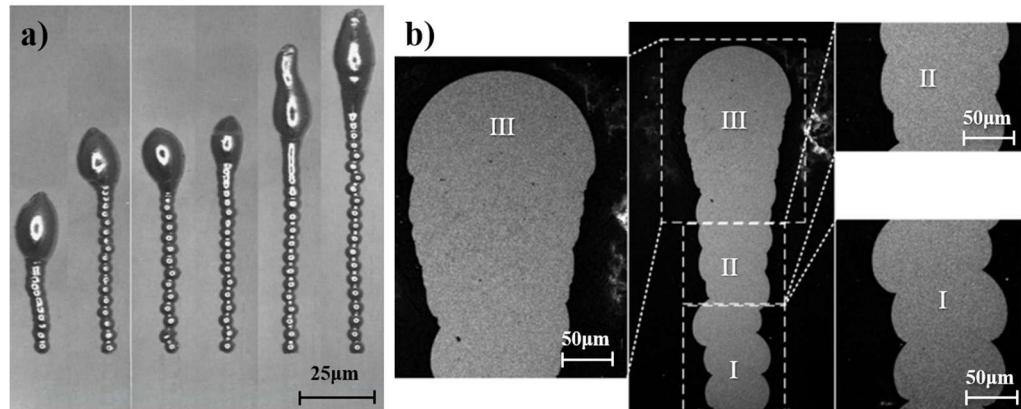


Figure 2.38 (a) heat accumulation effect (b) three stages of heat accumulation, divided into regions I to III.

- **Late Deposition Stage (Region III):** In the final stage of deposition, heat dissipation becomes constrained by the elongated heat transfer path and the thermal properties of the previously deposited layers. The extended solidification time may lead to over-remelting, causing droplets to merge

and form larger conglomerates, which can compromise the geometric integrity of the structure as shown in Figure 2.38(b) region III.

Adjusting process parameters such as substrate temperature, nozzle temperature and jetting frequency has been reported as a solution to this vertical heat accumulation problem. Fang, et al. [122] effectively increased the vertical deposition height by reducing substrate temperature and droplet temperature. However, these adjustments decreased the inter-droplet bonding strength and showed a higher risk of inner pore formation. Liu, et al. [123] proposed dynamically adjusting the deposition frequency according to the cumulative layer height, where a lower deposition frequency was applied when piling up, giving more time for the droplet to fully solidify. The drawback of this method was the increased printing time due to the decrease in frequency.

2.4 Materials development

Solder materials

As previously mentioned, historically, MMJ systems were developed for constructing solder circuits. Over time, these systems have demonstrated proficiency in printing a variety of low-temperature solder materials, as detailed in Table 2.1. Among these, the solder material with the highest melting point is pure Sn, which has a melting point of 231.9°C. Studies [45], [52], [53], [54], [56], [59], [62], [64], [65], [78], [124], [125], [126], [127], have consistently shown that Sn or solder droplets can be generated uniformly and stably. Furthermore, solder bumps and traces have been successfully printed, showcasing MMJ's capability to fabricate 3D printed circuits. The resolution of these printings ranges from 50µm to 600µm, depending on the specific system configuration employed.

Table 2.1. Solder materials that were successfully developed in MMJ systems in a time sequence

Author	Year	Solder Materials	Melting Point (°C)	Resolution (µm)
Marusak [52]	1993	Indalloy-58	138	70
Liu and Orme [56]	1999	Sn63Pb37	183	120
Yamaguchi et al. [54]	2000	Bi-Pb-Sn-Cd-In	47	200
Cheng, et al. [62]	2005	Sn	232	600
Lee, et al. [60]	2008	Sn63Pb37	183	150
Yokoyama, et al [59]	2009	Sn-3Ag-0.5Cu	170-190	68
Luo, et al. [126]	2012	Sn60Pb40	183-190	700
Suter, et al [125]	2012	Sn	232	800
Tropmann, et al. [64]	2012	Sn95Ag4Cu1	217	180
Lass et al. [66]	2013	Sn95Ag4Cu1	217	180
Rumschoette et al. [53]	2016	Sn63Pb37	183	110
Luo, et al. [78]	2017	Sn60Pb40	183-190	300
Han, et al. [127]	2017	Field's metal	60	160
Simonelli, et al. [45]	2019	Sn	232	50

The microstructure of MMJ-printed Sn parts has been the subject of investigation in studies by Idell et al. [128] and Simonelli et al. Both studies observed that the crystal grains of MMJ-printed Sn droplets are irregular in shape and vary in size. The phenomenon is attributed to thermal cycling during droplet deposition, where droplets deposited partially remelt those that had previously solidified and quickly cool down to the substrate temperature. This interaction affects the consistency of the droplet's crystal structure [45], [128].

Aluminium, aluminium alloys and bronze

MMJ systems expanded their capability to include structural materials such as aluminium, aluminium alloys, and bronze soon after it was developed. Printing these structural materials brings additional challenges. To ensure adequate bonding between droplets, inter-droplet remelting is generally required, which typically demands nozzle temperatures in the range of 800–1000 °C. Operating at such high temperatures places stringent requirements on the thermal stability of the nozzle, the durability of isolators and sealing materials, and the capacity

of the cooling system. One of the earliest structural materials explored was pure aluminium, initially investigated by Orme and Smith [57]. They highlighted the importance of preventing aluminium oxide formation during droplet generation. Early investigations into aluminium MMJ [57], [129] identified challenges such as unmelted droplet splat boundaries, leading to internal porosity and weak inter-droplet bonding. Although these parts maintained geometric accuracy, their mechanical properties were compromised by these bonding issues. Subsequent studies have addressed these problems by refining printing parameters [110], [111], [119], which will be discussed in more detail in the section on MMJ process parameters.

Aluminium alloys, known for their enhanced corrosion resistance and superior mechanical properties compared to pure aluminium, are particularly suited for fabricating structural parts. Himmel et al. [118] fabricated parts from 4047A aluminium alloy using a pneumatic MMJ system, linking tensile strength to the quality of inter-droplet bonding. The study found that remelting at droplet boundaries could enhance tensile strength. Laderio et al. [130] manufactured parts from Al-4008 (Si 7% and Fe 0.08%) using the XeroElemX MMJ system and investigated the effects of ageing heat treatment on tensile strength and micro-hardness. The treatment was shown to improve tensile properties significantly by promoting silicon particle coalescence and precipitating iron-rich IMCs. Wang et al. [131] explored phase segregation in Al96In4 droplets, noting that aluminium phases tend to nucleate at the droplet's base, while indium-rich phases concentrate at the top during cooling. Their study adjusted droplet and substrate temperatures to minimise this segregation, enhancing material uniformity. Zuo, et al [117] used 7075 aluminium and identified optimal parameters for remelting inter-droplet interfaces, observing improved tensile strength.

Bronze has also gained attention as a crucial structural material. Ploetz et al. [132] examined the MMJ printing of CuSn8 and CuSn1 bronzes, optimising substrate temperatures to reduce porosity. Traxel et al. [133] investigated the printing of C95400 bronze, a popular alloy in marine applications. This study investigated the changes in microstructure and element distribution during MMJ

printing of alloys with more than two elements. A heat treatment is determined and is found to provide products with higher strength.

In addition to aluminium and bronze, zinc alloys such as Zn96Al4 have attracted interest for their robust strength, toughness, and wear resistance. Amirzadeh et al. [86] successfully generated droplets of Zamac 3 (Zn-4%Al-0.04%Mg) but encountered difficulties in forming stable jets and selecting compatible substrates for printing structures. Lass et al. printed Zn96Al4 at a nozzle temperature of 420°C [66], successfully creating thin-walled cylinders and micro-springs with high geometric integrity, although the study did not delve into the microstructure and mechanical properties.

High melting point materials

Materials with high melting points, such as Cu ($T_m = 1085^\circ\text{C}$), Ag ($T_m = 962^\circ\text{C}$), and steel ($T_m = 1370\text{-}1593^\circ\text{C}$), present significant challenges due to their demanding temperature requirements for both jetting and deposition. Zhong et al. successfully melted Cu in a pneumatic MMJ system at 1200°C and investigated the optimal pulse for droplet generation [84]. While no 3D parts were fabricated, the study marked a significant advancement as it was the first instance where uniform Cu droplets were generated and collected in MMJ. In another study, Gilani et al. explored the MMJ printing of Cu droplets onto various substrates (Al_2O_3 , AlN, Cu) using a MetalJet system [77]. These substrates varied in thermal conductivity, wettability, and surface roughness. Notably, there was no remelting observed at the droplet-substrate or droplet-droplet interfaces, with inter-droplet bonding proving stronger than droplet-substrate bonding. The bonding mechanisms varied by substrate: van der Waals forces with Cu, capillary forces with AlN, and diffusion bonding with Al_2O_3 . Despite challenges related to jetting duration, the study successfully printed 3D walls on a Cu substrate, maintaining excellent geometric integrity and achieving electrical conductivity close to that of bulk Cu.

Known for its high electrical conductivity and ductility, Ag was successfully jetted and formed into 3D samples by Simonelli et al. using the MetalJet system [45]. The study observed visible gaps and pores among the deposited droplets, which could not be eliminated through heat treatment.

Moqadam et al. tackled the challenges of jetting steel (100Cr6), which has a melting point of 1560°C, using a pneumatic MMJ setup [68]. The study highlighted the need to account for the expansion of cold inlet gas when it reaches the hot cartridge, which is crucial for high-temperature droplet generation. Although the revised pulse was effective for droplet generation, the study was limited to this phase with no further deposition or printing explored.

2.5 Toolpath planning

Toolpath planning in MMJ systems can generally be categorised into two fundamental approaches: vector-based and raster-based toolpaths [134], [135]. Each method offers distinct advantages and constraints, which are pivotal in shaping their applications and effectiveness in different printing scenarios.

Vector-based toolpath planning

Vector-based toolpath planning involves guiding the deposition head along continuous linear or curved trajectories. This method defines the toolpath with a series of vectors, each representing the precise coordinates and direction for segments of the print. The printhead follows these vectors in a seamless motion, depositing material in line-based patterns, as illustrated in Figure 2.39(a). Vector-based toolpaths are prevalent in both experimental [59], [61], [78], [136], [137] and commercial MMJ systems [72]. Same as its advantages in applying to other 3D printing technologies like FDM and LPBF, this approach is particularly effective for creating large continuous areas, thin walls [138], [139], and contour structures in MMJ [74] due to its efficiency and smooth material laydown.

However, this method encounters limitations when depositing discrete structures, as shown in Figure 2.39(b), or when working with small features whose size is close to the diameter of droplets, which may result in decreased accuracy unless sophisticated printing strategies are employed [139], [140], [141]. Additionally, inferred from its performance in LPBF, its application in multi-material interfaces may show limited potential [12].

The hardware requirements for implementing vector-based toolpaths are relatively modest, enhancing their adoption in commercial systems. The primary challenge lies in ensuring precise synchronisation between the stage actuators, especially during acceleration and deceleration phases, necessitating high-precision control and rigorous calibration of the system's linear stages.

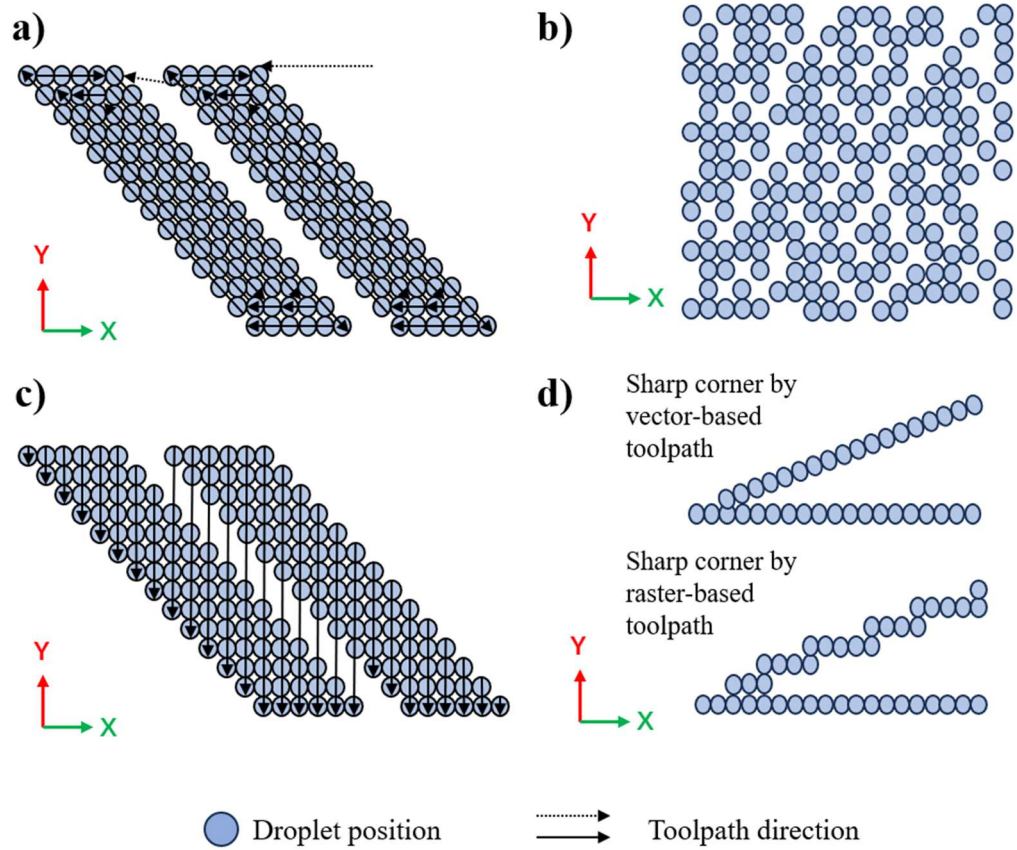


Figure 2.39 Toolpath planning example of (a) A typical vector-based toolpath planning, (b) A discrete pattern with detailed features which is not suitable for vector-based toolpath planning, (c) A typical raster-based toolpath planning example, (d) A sharp-corner structure with feature size close to or smaller than droplet diameter.

Raster-based toolpath Planning

Raster-based toolpath planning, also known as voxel-based or pixel-based, involves directing the material deposition head to specific, predetermined coordinates, aligning with a grid pattern across the print bed. This method deposits material in discrete droplets or "pixels", with the printhead moving in a raster pattern to lay down these droplets sequentially, as shown in Figure 2.39(c). Raster-based planning is favoured in multi-material inkjet printing and

full-colour 3D printing, where it allows for the precise placement of differently coloured materials [142], [143].

In MMJ systems, raster-based toolpaths, such as those used in the MetalJet system [45], are particularly beneficial for printing high-resolution textures and intricate geometries involving discrete droplet deposition. Despite its advantages in multi-material printing, this method is less efficient than vector-based planning for large contour patterns. The defined raster grid can also compromise accuracy when the feature size approaches the droplet size [144], as illustrated in Figure 2.39(d), making it suitable for circumstances where the droplet size is equal to or smaller than the desired feature size.

Implementing raster-based toolpaths requires hardware capable of rapid processing and high-frequency operation. Controllers with minimal delay times and high communication frequencies are crucial, often employing expensive high-speed In-Out modules such as Field Programmable Gate Arrays (FPGAs) and high-accuracy position sensors to achieve precise control and maintain high fabrication speeds [145], [146].

Advanced toolpath planning and deposition strategies

Besides the two traditional toolpath planning methods, some more advanced toolpath planning and deposition strategies have been developed in MMJ systems to enhance the final product's geometry integrity, surface roughness and density.

Dou et al. [139] introduced a novel toolpath planning algorithm aimed at accurately restoring the geometric features of thin-walled parts. As illustrated in Figure 2.40(a), they categorised corner features into two regions: the arc branch area (A) and the fan-shaped area at the vertex (B). The arc branch area is treated as a rectangular zone where droplets are arranged along its two sides following traditional vector-based toolpath planning. Conversely, the fan-shaped vertex area is segmented into several arcs with a defined droplet spacing (ds). Here, droplets fill the arcs to ensure complete coverage of the area using a layer-by-layer concentric ring approach, depicted in Figure 2.40(b). For complex fan-shaped areas, positional adjustments of droplets within their respective circular sectors are necessary to distribute filling errors uniformly, as shown in Figure

2.40(c). This strategy allows for efficient printing without the need for additional tool tracks.

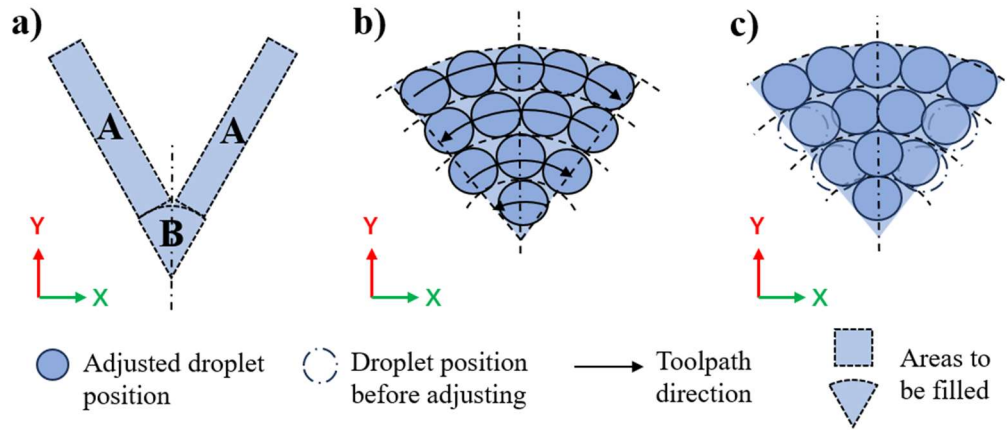


Figure 2.40 Diagrams of the “Vertex-Arc” toolpath planning method: (a) A thin-wall corner is divided into an arc branch and a fan-shaped area at the vertex, (b) Droplet arrangement method in the fan-shaped area and the toolpath for filling this area, (c) droplet position revision within each arc.

Aimed to print at high substrate temperature and nozzle temperature, Luo et al. [141] implemented an alternate deposition strategy designed to create uniform traces in MMJ. This approach involves two printing phases: the initial phase deposits every other droplet along the trace, leaving spaces, as indicated by "1" in Figure 2.41(a). The subsequent phase then fills these gaps, forming a complete trace, marked as "2" in the same figure. This method ensures that droplets from the first print solidify before making contact with adjacent droplets, preventing droplet coalescence at high-temperature substrates.

Inspired by the texture of composites that enhanced the strength of the material, Watkins et al. [140] explored the impact of varying inter-layer trace directions on the tensile strength of the final parts. They examined trace directions parallel, perpendicular, and crosshatched, as shown in Figure 2.41(b). Although variations in tensile strength were observed, they attributed these differences to the unique deposition technique, where each droplet is deposited onto a partially solidified previous droplet, resulting in smooth traces with inter-trace porosity. This method, however, significantly reduces single-trace resolution and is not recommended for general use.

To optimise side surface quality, Qi et al [147] conducted a topology analysis to determine the necessary filling space for each droplet along and between printing traces. The study suggested that ds within a trace ($ds-X$) should differ slightly from that between traces ($ds-Y$), as demonstrated in Figure 2.41(c). This strategy was proven effective, showing a reduced surface roughness compared to conventional methods. A subsequent study by the same group [148] indicated that orienting the print side surface at a specific angle could further reduce surface roughness, achieved by shifting the deposition layers. However, this method restricts design freedom due to limited permissible angles for side surfaces.

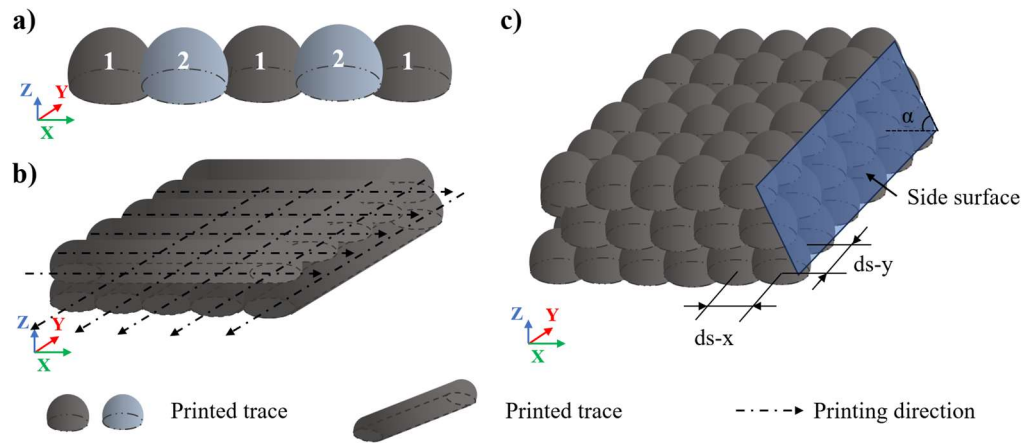


Figure 2.41 (a) “Alternate” strategy of printing a trace, droplets marked “1” print in the first scan and those marked “2” print in the second (b) Trace printed in different directions (c) The ds within the trace $ds-X$, spacing between the traces $ds-Y$ and side surface with tilt angle.

2.6 MMJ application

Cu traces printed by MMJ can achieve $6.75 \times 10^{-8} / \Omega m$, which is only 3.8 times the electrical resistance compared to pure bulk Cu ($1.77 \times 10^{-8} / \Omega m$). Successful applications of printed electronics using MMJ include conductive traces [126], circuits [149] and a horn antenna with 5cm in height [150], [151], [152], as shown in Figure 2.42(a)-(b).

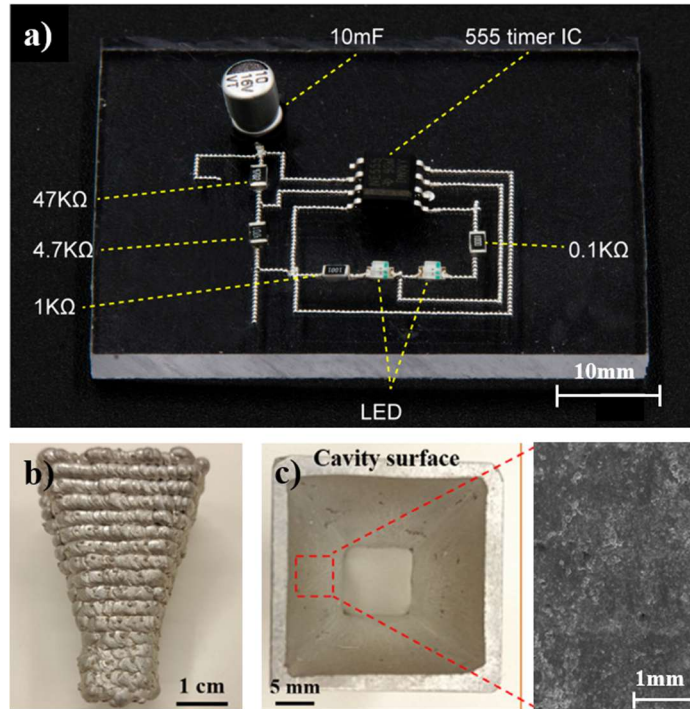


Figure 2.42 (a) Diagram of a recyclable circuit with a capacitor, a resistor and LEDs, adapted from [149] (b) Photographs of horn antenna printed on dissolvable polymer, adapted from [150] (c) Photographs of its smooth inner surface of the horn-shaped part and an SEM image of the inner surface, adapted from [150].

MMJ showed potential in printing in zero-gravity environments [153]. In this application, low-gravity conditions were simulated by positioning a piezoelectric actuated printhead horizontally and depositing droplets onto a vertically oriented substrate, as demonstrated in Figure 2.43(a). To counteract the effects of gravity, an electric field was introduced [154], [155]. Despite the successful compensation for gravity during droplet flight, the effects of gravity on the droplet solidification process were still noticeable, often resulting in droplets with irregular shapes and finally increasing the surface roughness of the final product [156]. Thin walls have been printed using the technique, as shown in Figure 2.43(b-d).

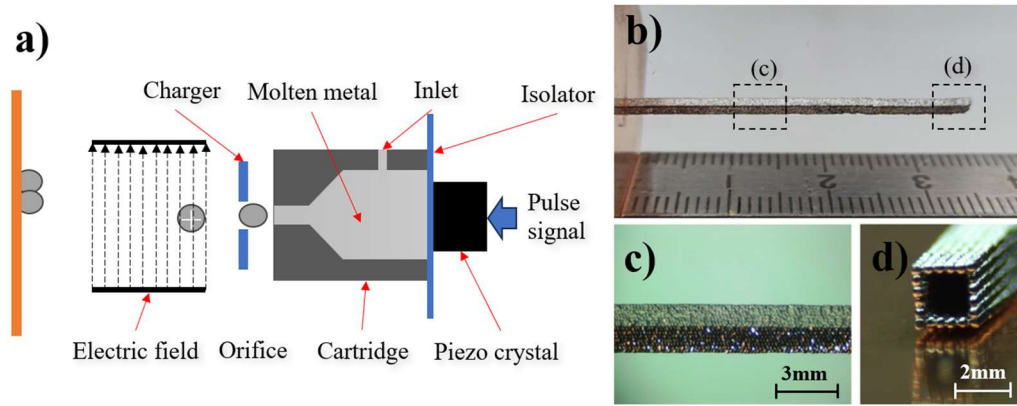


Figure 2.43 (a) Diagram of the setup emulating printing in low-gravity environments, adapted from [153] (b)-(d) Photographs of thin-wall pillars, adapted from [156].

Printing overhang structures remains a significant challenge in AM. In MMJ, two approaches have been developed to either eliminate the need for supports or use dissolvable supports effectively. Kumar et al [157], [158] explored the printing of free-hang slopes at various tilting angles, as illustrated in Figure 2.44(a). By adjusting the droplet spacing (ds), they successfully demonstrated the capability to print supportless lines with tilt angles as steep as 30° . Additionally, lattice structures were produced, showcased in Figure 2.44(b). Kirchebner et al [71], [159] utilised printable and dissolvable supports for fabricating overhang structures. Drawing from their research on salt printing [70], they selected a combination of NaCl-KCl for the support material and aluminium for the structure, with the process displayed in Figure 2.44(c).

Both approaches offer distinct benefits and drawbacks. Adjusting droplet spacing enables the fabrication of overhang structures without the need for additional supports. However, this method is limited by the minimum achievable tilt angle, which depends on the material used as well as printing conditions such as nozzle and substrate temperatures. These constraints can limit design flexibility. In contrast, the use of printable, dissolvable supports allows for greater design freedom but introduces challenges related to the thermal conductivity and wettability of the support materials. To date, no dissolvable material has successfully combined both adequate thermal conductivity and wettability.

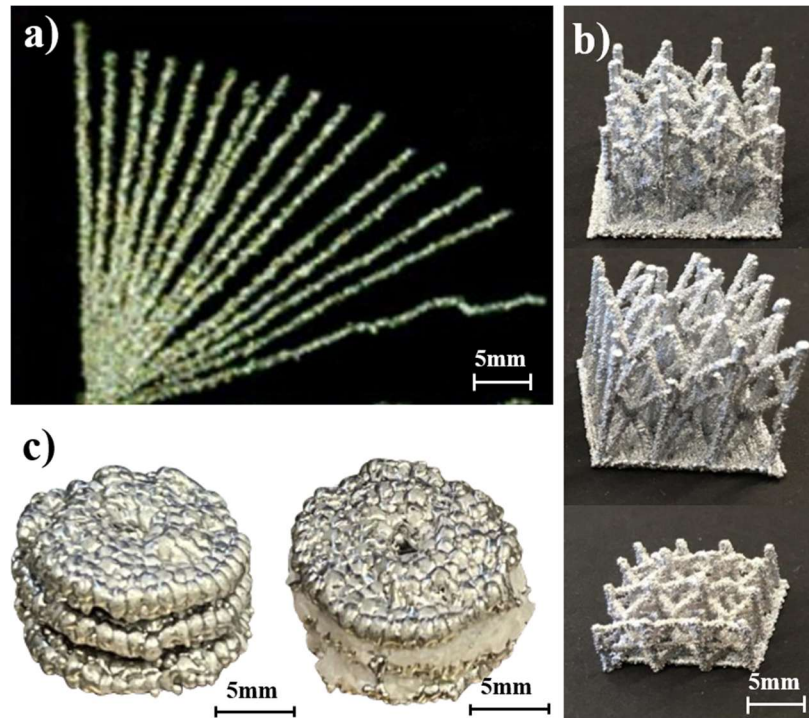


Figure 2.44 (a) Photographs of an overhang tilt line printed by adjusting ds , adapted from [157], [158] (b) Photographs of lattice structures (c) Photographs of a part with an overhang feature printed with salt as support, adapted from [71], [159].

MMJ extends beyond traditional applications on substrates, also enabling the printing directly onto existing parts to add fixing or joint features. This method can be particularly beneficial for integrating additional structural elements or for repair purposes. Yang, et al [160] demonstrated Al printing on a Ti frame as illustrated in Figure 2.45(a-b). The Ti frame acts as a substrate, and the combination product can achieve zero thermal expansion. Another case is the MMJ repairing conducted by Kirchebner et al [161]. Al droplets were deposited onto a cast aluminium structure that had a notch for repairing, as shown in Figure 2.45 (c). Despite the deposition being accurate, the tensile strength tests after heat treatment revealed that the repaired part did not achieve the same strength as the original cast component. This shortfall was attributed to tiny gaps at the repair interface and inadequate bonding between the newly deposited material and the original part, highlighting the challenges in achieving full restoration of mechanical properties through MMJ-based repairs.

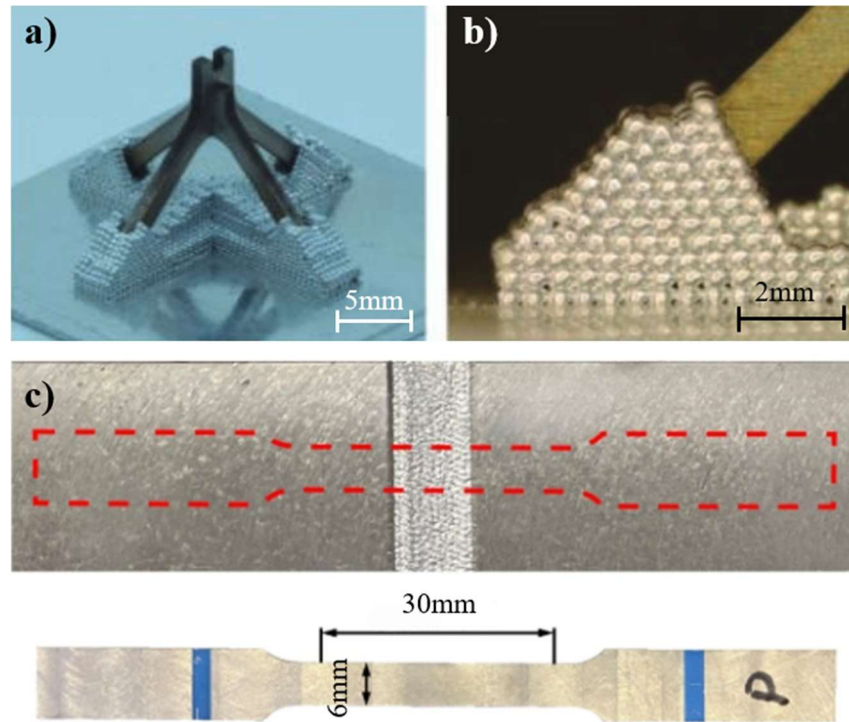


Figure 2.45 (a) Photo of printed Al base with forged Ti frame, (b) Photograph of the corner of the printed Al base, (c) repaired cast Al part with MMJ printed notch.

3 Materials and methods

This section details the materials and experimental methods employed in this research. It begins with an overview of the dual-head MetalJet system developed during this study, followed by a description of the jetting and substrate materials. The experimental procedure is then outlined, accompanied by a flowchart illustrating the process. Finally, the characterisation techniques used to analyse the printed samples are presented. The overall research workflow is summarised in Figure 3.1.

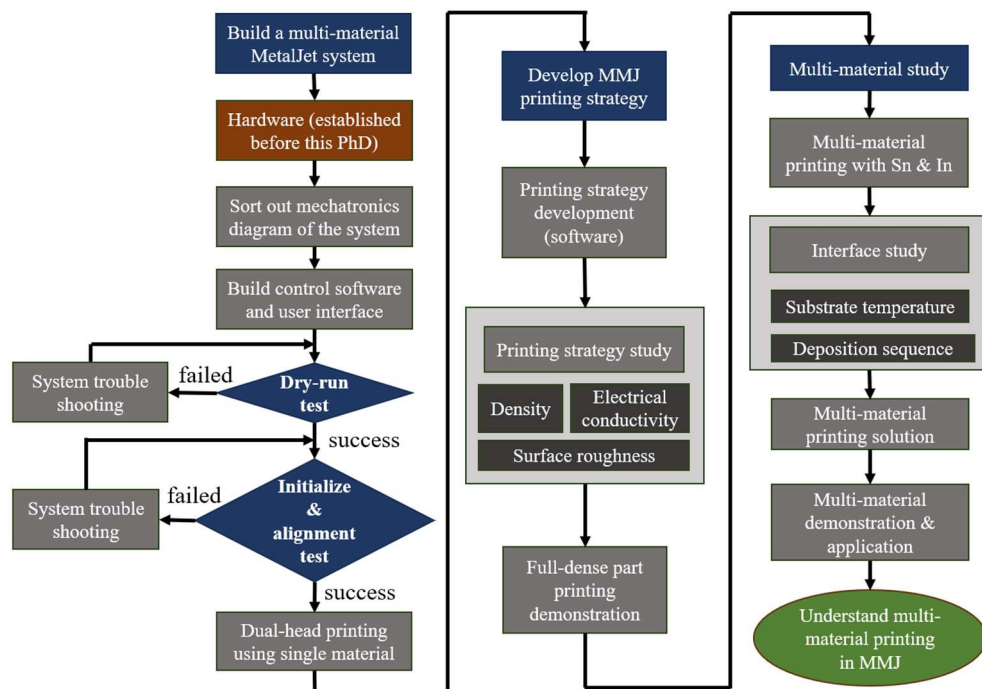


Figure 3.1 Research flowchart.

3.1 Dual-head MetalJet system

The subsequent sections detail the developmental stages of the dual-head MetalJet system, including hardware setup, mechatronics system, multi-material printing procedures, and software design and system troubleshooting during the developmental stages.

3.1.1 System introduction

The dual-printhead Molten MetalJet system was engineered by modifying the existing single-printhead configuration [45]. As shown in Figure 3.2, the newly designed system is structured into three main sections: the front-end assembly, the back-end electronics, and the user interface area. To be clear, though, without control software or a user interface, the hardware framework and most of the equipment were established before this PhD.

Front-end Assembly:

This section forms the heart of the printing operations, featuring two printheads that manage metal melting and jetting. It includes a building platform equipped with XYZ linear stages (Aerotech A3200) to support precise substrate movement. For monitoring jetting quality, a JetXpert stroboscopic camera (ImageXpert Inc., New Hampshire, USA) is employed, alongside an industrial camera for calibration purposes. The entire assembly is housed within a glovebox (MBRAUN Lab master Pro) to maintain controlled levels of oxygen and moisture, essential for preventing oxidation during the printing process. Water cooling circuits are installed for both printheads and the substrate to effectively manage heat dissipation.

Back-end Electronics:

This area houses the vital control and power components of the system. It includes a waveform generator, a substrate temperature controller, a high-frequency generator, a PC, an embedded lower-computer, and current amplifiers. To enhance safety, low-voltage devices such as waveform generators and controllers and high-voltage devices such as voltage magnifiers and relays are distinctly segregated into two separate compartments, indicated by the red and green regions in Figure 3.2.

User Interface Area:

Located in the yellow area of Figure 3.2, this section comprises monitors, a keyboard, and a mouse, providing operators with comprehensive control and monitoring capabilities. This setup ensures that users can efficiently manage and observe all aspects of the printing process

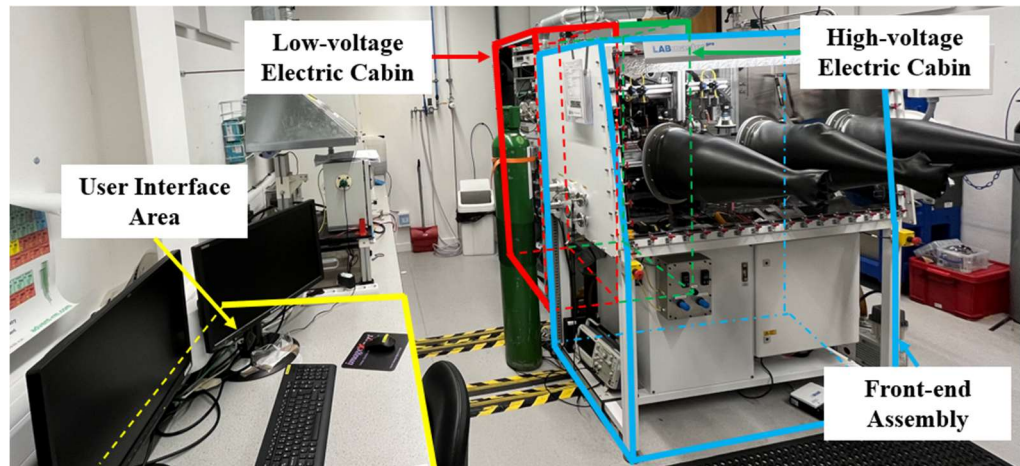


Figure 3.2 The frontend assembly, backend electronics (low-voltage cabin and high-voltage cabin) and user interface area of the dual-head MetalJet system diagram.

3.1.2 Mechatronic diagram

Before this PhD research, although parts of the electronic system had been established, the absence of control software rendered the platform unsuitable for any multi-material printing tasks. The work undertaken in this research involved completing the electronic integration, building up the control software and troubleshooting the system.

The configuration of the dual-head MetalJet system is illustrated in Figure 3.3. The control software is built using LabVIEW (2013). A National Instruments FPGA module functions as the lower computer. The FPGA operates at a maximum frequency of 50 MHz, allowing high-speed digital and analogue input/output operations. The mechatronic architecture comprises a combination of FPGA–PC hybrid control modules and fully PC-based control modules, each designed to manage different operational functions. These modules coordinate all electronic subsystems and collectively support the requirements of multi-material MMJ.

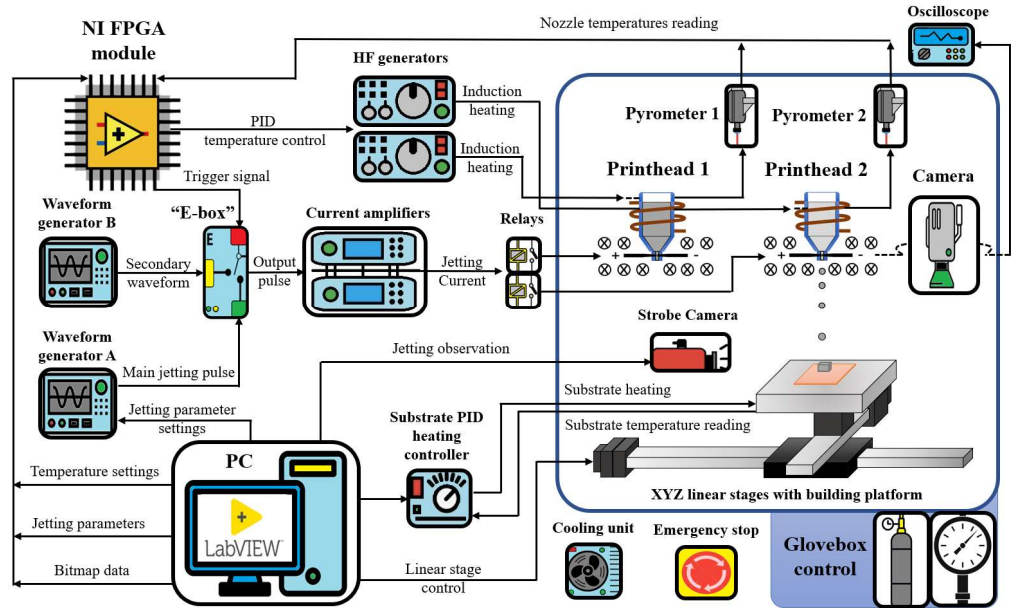


Figure 3.3 System diagram of dual-head MetalJet system

The key control modules are:

1. Cartridge heating module

Each printhead cartridge is preheated via a high-frequency generator at the experiment's commencement. As demonstrated in Figure 3.3, nozzle temperatures are monitored by pyrometers, with data fed back to the FPGA, which also receives temperature setpoints from the PC. A Proportional–Integral–Derivative (PID) closed-loop controller is used to regulate the temperature due to its precision, simplicity, and fast response. In the PID loop, the FPGA regulates these temperatures precisely by sending analogue signals to the generator. Additionally, two water-cooling circuits integrated within the printheads help manage heat, operated independently by a chiller outside this control loop.

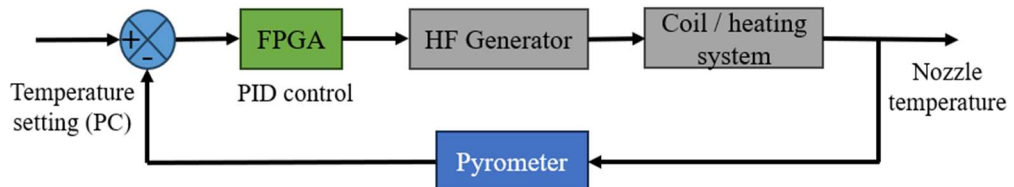


Figure 3.4 Block diagram of cartridge heating loop

2. Substrate movement module

In this setup, the position of the printheads is fixed while the substrate moves relatively to complete the printing. This module, as shown in Figure 3.5, initiates with a bitmap image loaded into the PC, which then calculates droplet positions and manages the platform's movement along the toolpath. The position of the building platform is precisely controlled by a closed loop using Aerotech A3200 stage encoder, whose data is read by the FPGA and passed to the main PC.

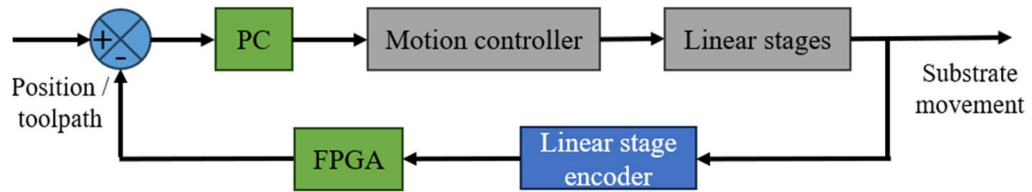


Figure 3.5 Block diagram of substrate movement loop

3. Pulse generation module (during printing)

The pulse generation module and stage movement loop work together to finish a printing. As mentioned in the previous loop, during the printing, the FPGA tracks position data from the stage encoder and issues a trigger pulse to the pulse manipulation device (referred to as “E-box” hereafter) at the precise droplet deposition point. This meticulous feedback mechanism ensures accurate droplet placement and synchronisation, particularly critical during stages of acceleration and deceleration.

Jetting waveforms comprise a primary jetting waveform and a secondary waveform for maintaining nozzle temperature. Before printing, Waveform Generator A loads a preset waveform, while Waveform Generator B produces a continuous sine waveform for localised nozzle heating. The E-box continuously emits this secondary waveform until a trigger pulse prompts it to switch momentarily to the main waveform for jetting. The pulse is then amplified by high-voltage amplifiers and applied uniformly across both printheads.

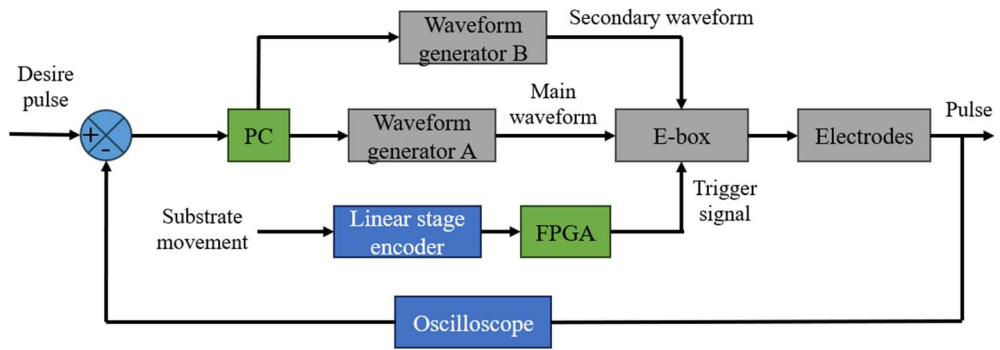


Figure 3.6 Block diagram of the pulse generation loop during the printing

4. Printhead switching module

Printhead selection is managed by two PC-controlled relays, which alternately activate and deactivate the printheads. The system simplifies positioning by referencing the printhead number and its relative position, ensuring the active printhead is correctly aligned over the building platform's centre, thus reducing potential for operator error.

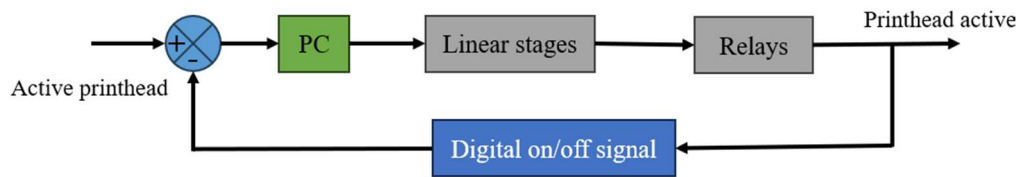


Figure 3.7 Block diagram of printhead switching loop

5. Jetting observation module

Centred around the JetXpert stroboscopic camera, this loop provides real-time data on droplet size, velocity, and trajectory, essential for monitoring and adjusting jetting quality, demonstrated in Figure 3.8. The stroboscopic camera has not yet been built into a closed-loop control system; thus, the adjustment in jetting parameters was decided by the operator based on the droplet data readings and images.

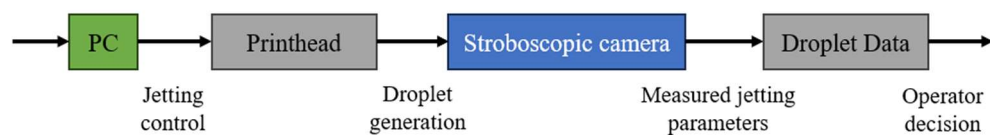


Figure 3.8 Block diagram of jetting observation workflow

6. Substrate heating module

An integrated substrate heater maintains the target temperature as set by the PC, ensuring optimal conditions for material deposition and solidification, as illustrated in Figure 3.9. To be noticed, this PID controller is built together with the substrate heater as an entire device, which means its control works outside either the PC or the FPGA.

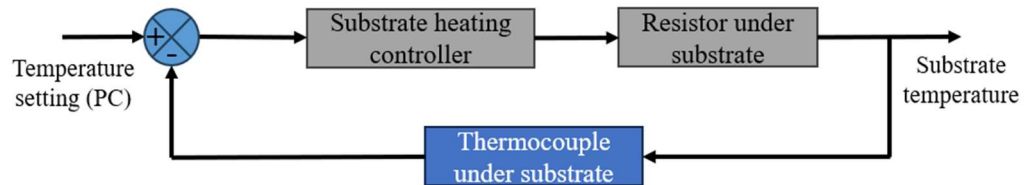


Figure 3.9 Block diagram of substrate heating loop

7. Calibration module

As displayed in Figure 3.10, utilising a downward-facing industrial camera, this loop is controlled via a LabVIEW calibration program that not only calibrates the system but also checks the quality of the printing. Same as the stroboscopic camera, this calibration camera has not yet been built into any in-situ control loops. The printing adjustments are decided by the operator, based on the measurements or images from the camera.

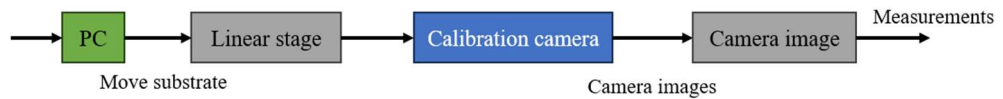


Figure 3.10 Block diagram of calibration workflow

3.2 Materials

Feedstock materials:

Tin (Sn): High-purity tin (Sn, 99.9998%) from Goodfellow was used as the feedstock material. A graphite cartridge coated with tungsten carbide (WC_2) is used to store the feedstock Sn and is then heated up to $680^\circ C$ to melt the material

[45], [46]. The substrate temperature was varied between 30 °C (ambient temperature in the MetalJet glovebox) and 200 °C.

Indium (In): The main reason to use Indium is that it has a good thermal compatibility with Sn, so they can form a material pair. Indium (99.999% purity) from Advent Research Materials was used as feedstock material. Considering that its conductivity, viscosity and wetting ability are close to Sn, a jetting temperature of 630°C is chosen. The substrate temperature is tested to be available from 30°C (environment temperature in the MetalJet glovebox) to 100°C.

Silver (Ag): High-purity silver (99.999%, ESPI Metals) was used as the feedstock material. To jet molten Ag, the cartridge was heated to 1050°C. The substrate temperature was set to 400 °C.

Substrate material: High-purity Cu (99.98%, CU1355, Advent Research Materials) was used as the substrate material. To prepare the substrates, 50 mm × 50 mm × 1 mm copper plates were cut into 20 mm × 20 mm × 1 mm substrates using electrical discharge machining (EDM).

3.3 Experiment methods

3.3.1 MetalJet experiments

The methodology for conducting MetalJet experiments is outlined by the flowchart in Figure 3.11. This flowchart segregates the experimental steps into distinct phases, highlighted by green boxes for pre-experiment preparations and blue and orange boxes for operations during the experiment. Initially, the cartridge is cleaned to remove any residues from its manufacturing process before installation. Both the substrate and feedstock materials are etched using a solution of 33% hydrochloric acid solution to remove surface oxides. Following etching, they were cleaned with a 1:1 solution of isopropanol and deionised water to ensure surface cleanliness. The substrates and feedstocks were then dried using high-purity nitrogen gas and put into the glovebox. The etching, cleaning and drying procedures were operated in an open-air

environment. The materials are then quickly sent to a glovebox whose environment is maintained below 0.1 ppm to prevent further oxidation.

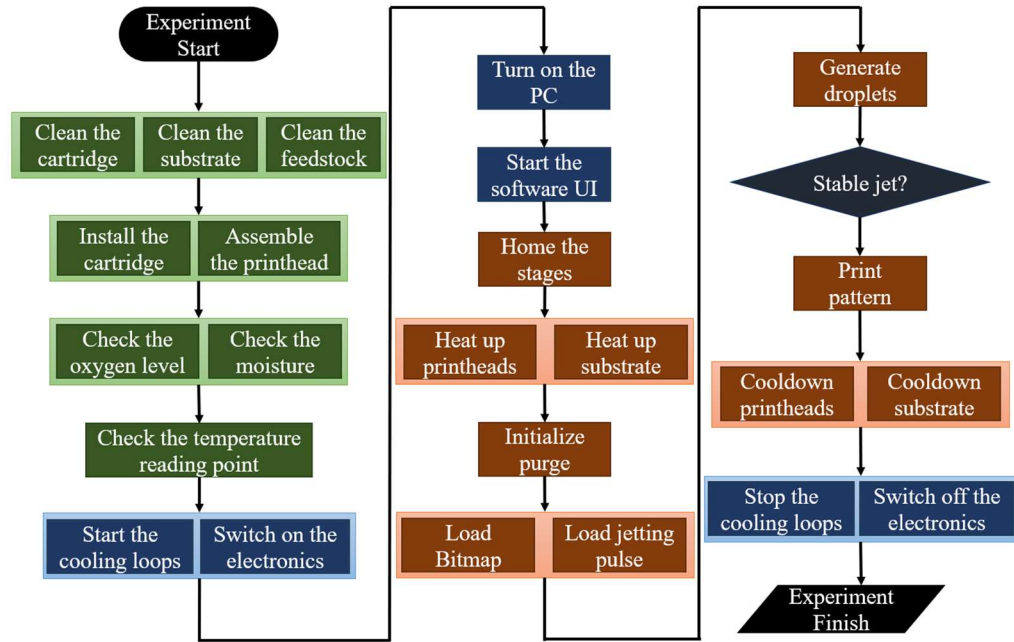


Figure 3.11 MetalJet experiment flowchart

Before starting the experiment, the operator should check the position of the nozzle. Referring to the print head structure shown in Figure 3.12(a), the correct position of the nozzle should be in the area between the two permanent magnets that provide the magnetic field for the nozzle, but not in contact with the two permanent magnets. When starting the experiment, the chillers and all electronic devices within the cabin are activated as a prerequisite for system operation. Then, the temperature reading point should be at one upper corner of the nozzle, as indicated in Figure 3.12(a). The cartridge is then heated using the control software by setting a target temperature and initiating the process via the green “Heat up Nozzle” button, shown in the white circle in Figure 3.12(b). Heating begins with a gradual heating at the increment rate of 0.8°C/s , shifting to PID control once the set temperature is reached. The printhead is then initialised by purging, indicated by a stable, long, tail-shaped figure on the strobe camera image. Following a successful purge, droplet jetting commences with pulses loaded and sent to the electrodes, adjusting the voltage, typically between 55-70 V, to maintain a droplet flying speed of 1 m/s. Finally, a pattern is printed using the software, effectively translating digital designs into physical metal

structures. This comprehensive approach ensures meticulous control over each stage of the experiment, enhancing the reliability and quality of the results.

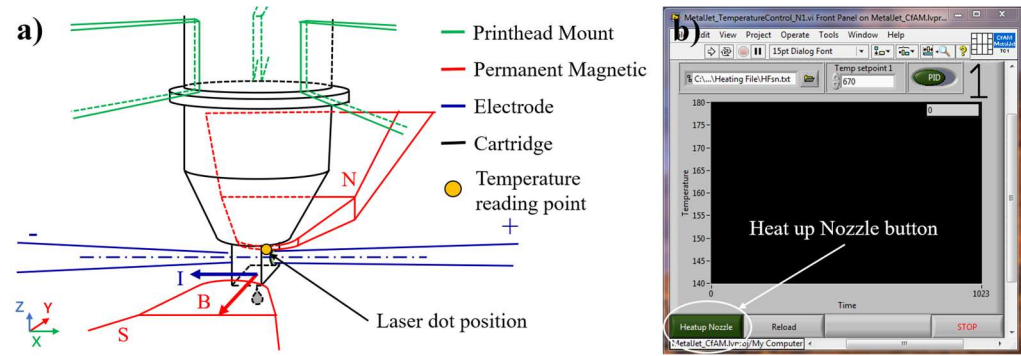


Figure 3.12 (a) Correct position of the laser dot (b) Cartridge heating software user interface

3.3.2 System development evaluation methods

To assess the dual-head MetalJet system's functionality, two initial tests were conducted using Sn and Ag, respectively. These tests aimed to evaluate several key performance criteria essential for effective MMJ operation:

1. Heating function: The system must consistently maintain the designated substrate temperatures throughout its operation, with target settings of 160°C for Sn and 400°C for Ag. This ensures that materials are processed under optimal conditions
2. Pulse generation: It is critical to verify that the correct pulse shape and voltage are applied during jetting. The applied jetting pulses are monitored using an oscilloscope connected to the electrodes, with different pulse types illustrated in Figure 3.13, purge pulses in blue dashed lines, Sn jetting pulses in black solid lines, and Ag pulses in red dashed lines.

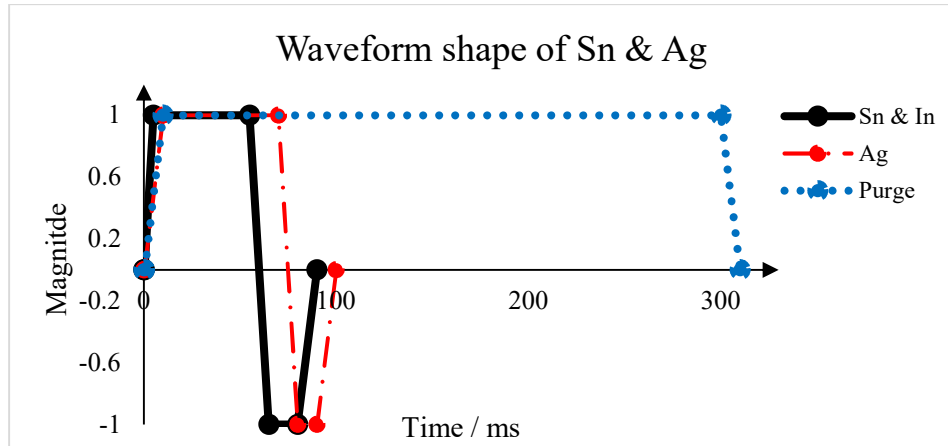


Figure 3.13 Waveform type of Purge pulse and Sn, In, Ag jetting pulse

3. Jetting Quality: Proper jetting is characterised by stable droplet velocity, diameter, and trajectory. These parameters are closely monitored using the JetXpert strobe camera to ensure consistent droplet formation and delivery.
4. Sample evaluation: A high-quality sample should display droplets precisely arranged according to the defined bitmap, without gaps, porosity, delamination, or stair-stepping effects.
5. Printhead alignment evaluation: To evaluate alignment, an experiment was conducted using Sn in both printheads to print a 3x3 checkerboard pattern. The same material in both printheads eliminates material-based discrepancies and focuses purely on alignment accuracy. Successful printhead alignment will see a seamless surface consisting of two checkerboard patterns.

3.3.3 Printing strategy study

Four distinct printing strategies were studied, named Normal, Staggering, Honeycomb and Alternate.

The first strategy shown in Figure 3.14 (a), referred to as "Normal," employs conventional square-shaped pixel packing based on a bitmap file. The second strategy, Figure 3.14 (b), "Staggering," shifts every other line from the Normal strategy by half a droplet distance in one direction, so that the protruding section of each droplet aligns with the concave regions formed by two droplets in the previous line. The third strategy, shown in Figure 3.14 (c), "Honeycomb", uses

regular hexagonal pixels, which are closely arranged like honeycombs in nature. The final strategy, "Alternate," involves initially depositing the droplets in a checkerboard pattern, followed by depositing the inverse checkerboard pattern to complete the layer, as depicted in Figure 3.14 (d). To be noticed, the Alternate strategy doubles the total printing time because the toolpath swipes the printing area twice to finish one layer.

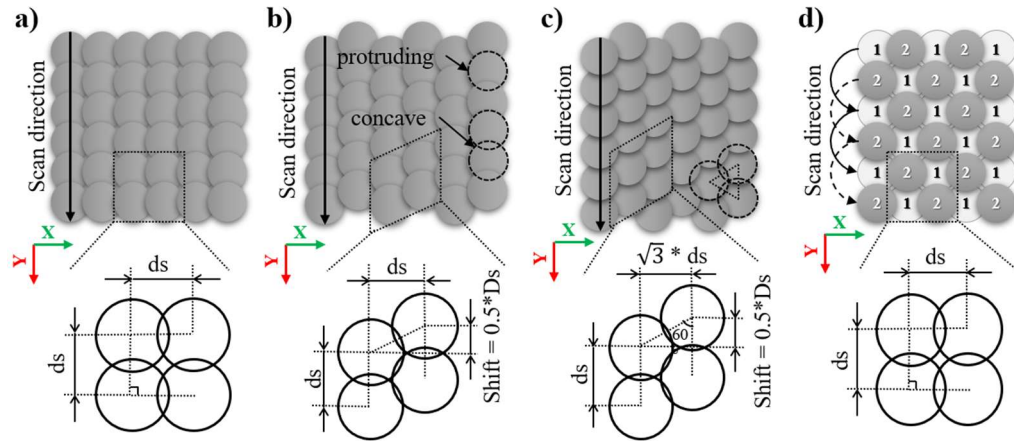


Figure 3.14 Diagram of four packing strategies (a) Normal, (b) Staggering, (c) Honeycomb, (d) Alternate, the droplet with number 1 marked will be deposited first round, and those marked with number 2 will be deposited in the second round.

Three substrate temperatures were evaluated: 50°C, 100°C, and 150°C, representing low, medium, and high temperature conditions (“high” being relative with respect to the melt point of the materials being deposited), respectively. Two types of samples are printed as demonstrated in Figure 3.15. Flat square samples of 50 droplets in length, 50 droplets in width, and 5 layers in height were printed for surface texture characterisation and density measurement. Long bars with cross-sectional areas of 5 droplets by 5 droplets and a height of 160 layers were printed for electrical conductivity measurements. To determine the ds_{opt} for each strategy at each substrate temperature, a series of samples is printed with droplet spacing (ds) values at intervals of 1µm, and a range centred at the estimated value.

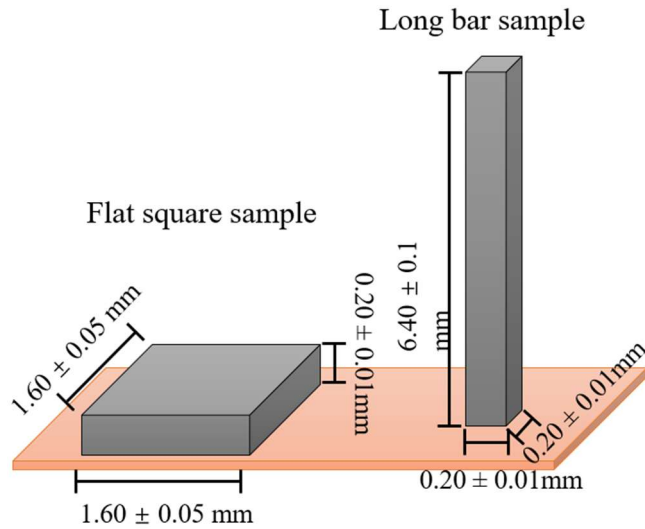


Figure 3.15 Two types of samples in a strategy study

3.3.4 Sn-In multi-material study

Printhead alignment was checked every two hours during the experiments, recognising that jetting consistency can affect alignment offsets. The alignment procedure involved printing a calibration array with both printheads at the same target location, applying the alignment offset. Successful alignment was confirmed when the two droplet arrays overlapped precisely; otherwise, the calibration was repeated to update the offset.

To study droplet behaviour at material interfaces, two types of samples were prepared. The first type, termed “droplet-by-droplet” samples, was fabricated using two deposition sequences. In the “In-first-Sn-second” sequence, Sn droplets were deposited alongside solidified In droplets. The reverse sequence, “Sn-first-In-second,” involved depositing In droplets adjacent to solidified Sn droplets. These samples were printed at substrate temperatures of 100°C , 80°C , and 60°C to assess the effect of temperature on interface formation. The second type, referred to as “droplet-between-droplets” samples, examined the influence of deposition ratio by placing a single droplet between two previously deposited droplets of different materials. These were printed at 100°C . In all samples, a $15 \mu\text{m}$ overlap between adjacent droplets was maintained to ensure consistent interfacial contact.

To demonstrate the system's capability for multi-material fabrication, an interdigitated structure was printed. The design ensured no direct contact between Sn and In materials. Considering the substrate temperature ranges for Sn (60 °C to 160 °C) and In (room temperature to 90 °C), a substrate temperature of 90 °C was selected to optimise printing quality for both materials.

3.4 Characterisation methods

This section describes the methods used to characterise sample microstructure, elemental distribution and concentration, cross-sections, internal porosity, and electrical conductivity. The techniques applied in this PhD research include SEM, EDX, FIB-SEM, CT, and four-terminal Kelvin resistance measurements.

3.4.1 Scanning Electron Microscope (SEM) & Energy Dispersive X-Ray (EDX)

The microstructure of the samples was analysed using a Hitachi TM3030 (Tokyo, Japan) SEM. SEM works by focusing a high-energy electron beam onto a sample surface under vacuum. As the electrons interact with the atoms in the sample, various signals are generated. These signals include secondary electrons (SE), backscattered electrons (BSE), and X-rays. The SE and BSE signals are detected and converted into images that reveal surface topology, composition, and structure. The beam is raster-scanned across the sample to build up a 2D image. The SEM is set to a working distance of 10 mm and a beam voltage of 20 kV.

The microstructure and element distribution of the samples were scrutinised using the integrated Energy Dispersive X-ray (EDX) element spectra on the Thermo Fisher (FEI XL30 SEM). EDX works by detecting the characteristic X-rays emitted as the electron beam triggers inner-shell electrons in the sample atoms. Element distribution and concentration can be figured by measuring the energy and intensity of these X-rays at the scanned region.

3.4.2 Focused Ion Beam (FIB)-SEM

The cross sections of the samples were prepared by Thermo Fisher FEI Quanta200 3D Dual Beam Focused ion beam SEM (FIB-SEM). The INCA Energy 250 Microanalysis System is integrated for EDX elemental spectra and mapping on the sections. This FIB-SEM system combines a focused Gallium ion beam with a scanning electron microscope. The FIB can mill away material through the sputtering process. As high-energy ions (usually 30 keV) are focused and directed onto the sample surface, they physically bombard the atoms in the target, transferring enough kinetic energy to eject surface atoms from the material.

The working distance for FIB and EDX is 15mm. To mill the section, raw milling is first applied. The ion beam at a current level of 20nA is used for raw milling. Then 7nA ion beam is used to clean the section. The ion beam energy for cleaning the section is further decreased to 5nA for fine milling and cleaning. The ion beam current level is chosen under the consideration of both efficiency and milling quality. The element distribution of the section was directly characterised by the integrated EDX system after the FIB was finished. To view the microstructure, the section is firstly exposed to a 1nA image for 10s and then uses a 30pA ion beam for imaging.

3.4.3 Computer Tomography (CT) scan and its data processing

The internal porosity, density and surface roughness were characterised by MicroCT employing a Zeiss Xradia Versa XRM-500 3D X-ray computed tomography (CT) system set to 160 kV and 63 μ A, and at 4X optical magnification. Multiple projection images were captured at different angles over a 180° range. These were then mathematically reconstructed into 3D models using a filtered back-projection algorithm using Zeiss Xradia Reconstructor™. The average pixel size was approximately 1.77 μ m for all samples, with 1601 projections per dataset. The reconstructed CT datasets were processed using a Dragonfly 3D Workstation (version 2024.1.0.1601). MATLAB is used to calculate the roughness value from the CT dataset. Figure 3.17 (a) illustrates the process of CT scan image analysis using the Dragonfly 3D Workstation.

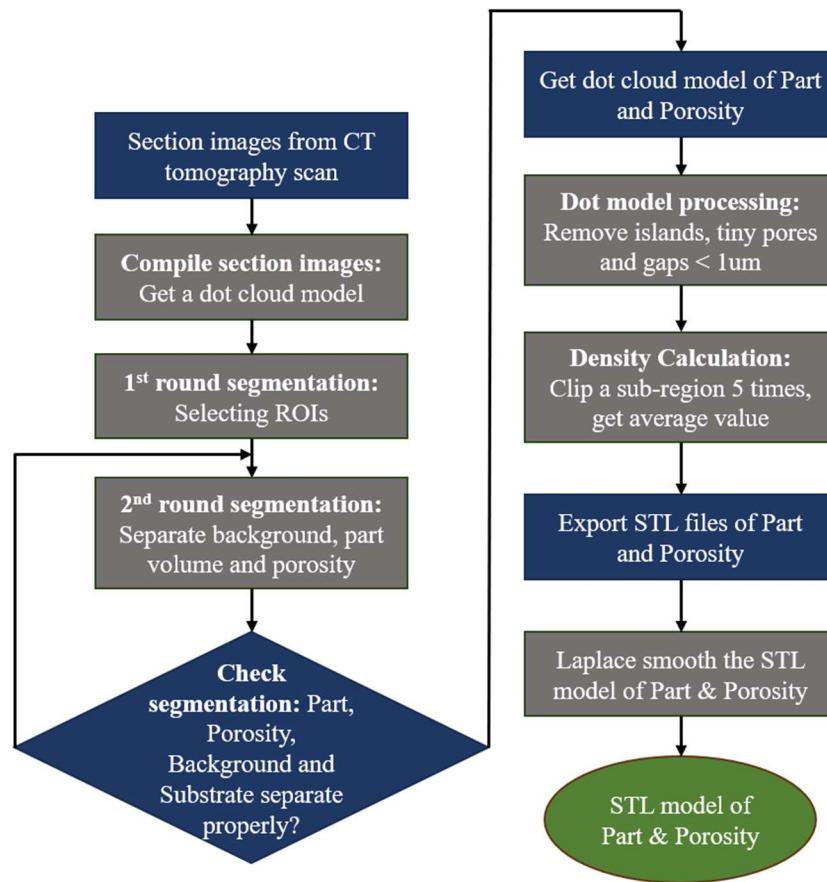


Figure 3.16 Flowchart of CT scan image processing, from raw data to dot cloud model to calculate density and finally export as STL file.

Initially, the raw CT images are compiled into a point cloud model, as depicted in Figure 3.17 (a). This model is composed of voxels represented in a grayscale range from 0 to 255. Segmentation tools are then employed to distinguish the part, porosity, and background, assigning each to a different region of interest (ROI) based on the grayscale values of individual voxels. An automatic segmentation is first applied, followed by manual adjustments to correct any misclassified voxels. Given the potential for errors in image processing, the point cloud models undergo further refinement to eliminate small, isolated regions, fill minor voids, and bridge gaps smaller than $0.1\mu\text{m}$. The resulting ROIs, as shown in Figure 3.17 (b), are Boolean point cloud models, with each voxel assigned either a true or false value based on its classification. Each dot cloud model was cropped five times from the second to the fifth layers, and the ratio of voids' volume to the entire sample volume was computed using the

voxel count method within the cropped regions. The density calculation is defined as:

$$\rho = \frac{V_{part}}{V_{part} + V_{porosity}} \times 100\% \quad (3.1)$$

where ρ is the density, V_{part} is the volume of the actual solid part and $V_{porosity}$ is the volume of extracted porosity from the post-processed data. In this study, V_{part} and $V_{porosity}$ are counted in number of voxels. Each sample was measured 5 times for average.

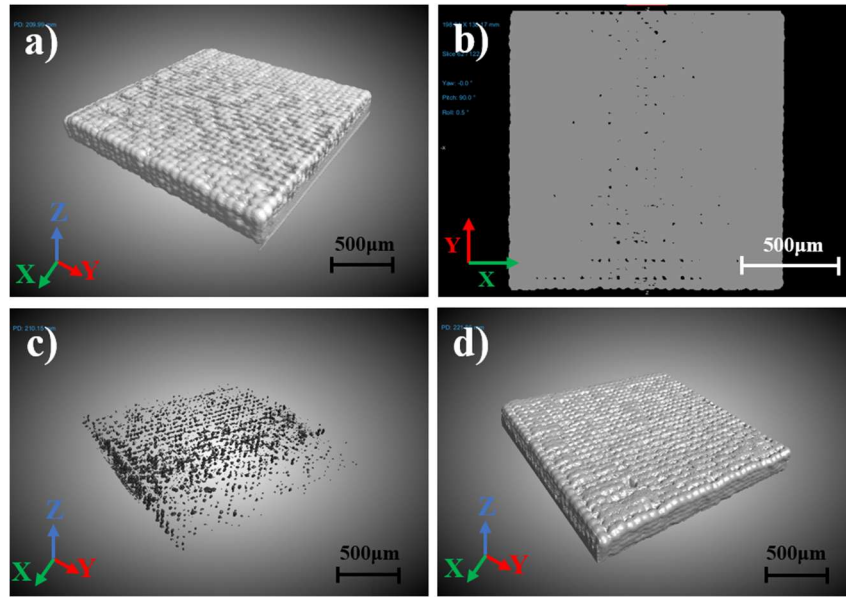


Figure 3.17 (a) Rendering of compiled CT scan image raw data (b) X-Y section view after segmentation and island processing (c) Smoothed 3D rendering model of porosity of middle layers (d) smoothed 3D rendering model of part

To better restore the top surface for surface roughness calculation, the ROIs were then transferred to STL files and smoothed 5 times using the Laplace smoothing method. The final STL file of the part and porosity is exhibited in Figure 3.17 (c)-(d), respectively. The STL file is sliced into 2 μm sections, with the image resolution adjusted so that each pixel represents a 2 μm x 2 μm area of the actual part. For each part, five samples are taken by selecting a 150 μm wide strip to reconstruct the surface. The surface reconstruction is achieved by identifying the first non-zero pixel along each vertical line in the sampled strip. This process is automated using MATLAB code. With the index of surface pixel

known in the section images, the surface height can be calculated, allowing for the calculation of the surface roughness average (R_a). The provided formula enables the determination of R_a based on the gathered surface data:

$$R_a = \frac{1}{n} * \sum_{i=1}^n |Z_i - Z| \quad (3.2)$$

where n is the number of slices, Z_i is the average height of the section i and Z is the average height value of the whole surface. The R_a value from 5 strips was then averaged to get the final surface roughness value.

3.4.4 4-terminal Kelvin electrical resistance measurement

To accurately measure the electrical resistance of printed multi-material structures, a 4-terminal Kelvin resistance measurement setup was employed. This method minimises the influence of contact and lead resistances, ensuring precise resistance readings. The measurement system consisted of a precision source meter and a set of four Tungsten probes positioned to make direct contact with the sample. Two outer probes supplied a constant current, while the two inner probes measured the resulting voltage drop across the structure, as shown in Figure 3.18. The resistance of the sample (R) at an effective length of (L) is:

$$R = \frac{U_I}{I_I} \quad (3.3)$$

where U_I is the voltage measured over effective length and I_I is the current measurement.

The electrical conductivity (σ_R) of the sample is calculated as:

$$\sigma_R = \frac{S}{R * L} \quad (3.4)$$

where S is the area of the cross section.

A Keithley 2400 source meter and a Keithley 7500 multi-meter are used to read the voltage and current values. All measurements were conducted at room temperature, and the setup was calibrated before testing to ensure reliability and repeatability of the results. Each sample was measured 5 times to get the average resistance value.

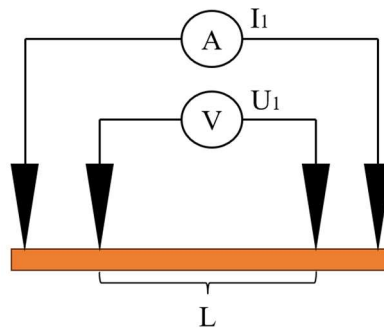


Figure 3.18 Diagram of 4-terminal Kelvin electrical resistance measurement

4 System development and evaluations

This section demonstrates the results of the system development. It includes the software and mechatronic system design, tuning, evaluation and troubleshooting.

4.1 Software design

A key contribution of this PhD project was the development of a control system and user interface for the dual-head MetalJet system. This section outlines the top-level design of the software, showcasing the overall concept and structural layout tailored to enhance both functionality and user experience.

4.1.1 Structural design

Upon a thorough understanding of the system's hardware and mechatronics, it became evident which functions need to be implemented and which devices are involved in each function. Practical experience from experimental operations has highlighted that strategically separating certain devices and functions can significantly enhance experimental success and user experience. This approach is particularly beneficial in scenarios where:

1. **Device Inactivity:** Some devices experience long periods of idleness during the printing processes. By turning these off when not in use, the burden on the main computer is reduced, conserving resources and improving system efficiency. For example, substrate heating is not activated when printing on a room-temperature substrate, and the motor for moving the LED strobe is only engaged when the camera switches between printheads.
2. **Device Reliability:** Older, more problematic devices benefit from isolation within the system. This separation allows for targeted restarts of specific components without necessitating a complete system reboot if they fail during an experiment. For example, the induction heater for printhead 1 exhibited reduced reliability, which on occasion resulted in sudden interruptions in heating.

Table 4.1 details the functions that the software needs to manage, along with the devices involved, considering both the duration of use and device reliability.

Table 4.1. Functions to realise the device's evaluation

Function	Devices involved	Idle time / overall printing time (%)	Accidents note	VI
Cartridge heating	Induction heater Pyrometer FPGA module	0%	Operate during the printing; the induction heater is old and sometimes fails	
Substrate heating	Substrate PID controller PC	< 5% when needed. But 100% when not needed	n/a	Main
Stage movement	Linear stages PC	< 5%	n/a	Main
Tune jetting	FPGA Waveform generator	0%	n/a	Main
Move the LED strobe	LED Stepper motor PC	> 95%	Rarely, but happens, jerks the overall input	LED Movement VI
Calibration camera	Camera PC	$\approx 70\%$	The camera will freeze the entire computer after hours of operation	Calibration VI

The software control architecture has been designed to comprise four distinct VIs. This arrangement includes consolidating the printing execution, stage control, and jetting tuning within a single user interface to streamline operations. Meanwhile, controls for the two nozzle temperatures, strobe camera movement, and calibration camera operations are managed through a separate user interface. This segmentation not only minimises simultaneous device communication, thereby reducing the processing load on older PCs, but also ensures that heating functions run independently. This independence is crucial for maintaining system stability, particularly if other programs crash or if multiple applications

compete for system resources. They also ensure the system's reliability and effectiveness, especially in such an experimental setup.

The layouts of the main user interfaces are illustrated in Figure 4.1 and Figure 4.2. The blue rectangle at the top is the system status indicator, which informs the operator when an operation or process has been completed. The blue rectangle at the bottom displays the error window alongside the linear stage position indicator. The dashed brown rectangle at the bottom represents the substrate heating control panel, which manages both the target temperature setting and the current substrate temperature display. The black dashed rectangle contains a tab controller that switches the interface between “Motion Control” and “Print Bitmap”. Figure 4.1 shows the interface in “Motion Control” mode, which comprises three function panels marked in green dashed rectangles. The left panel provides basic controls for enabling, disabling, and homing the linear stages. The upper panel allows the substrate to be moved to pre-calculated positions, such as under the printheads or under the calibration camera. The lower green panel provides basic linear stage motion control, enabling a selected stage to move a specified distance.

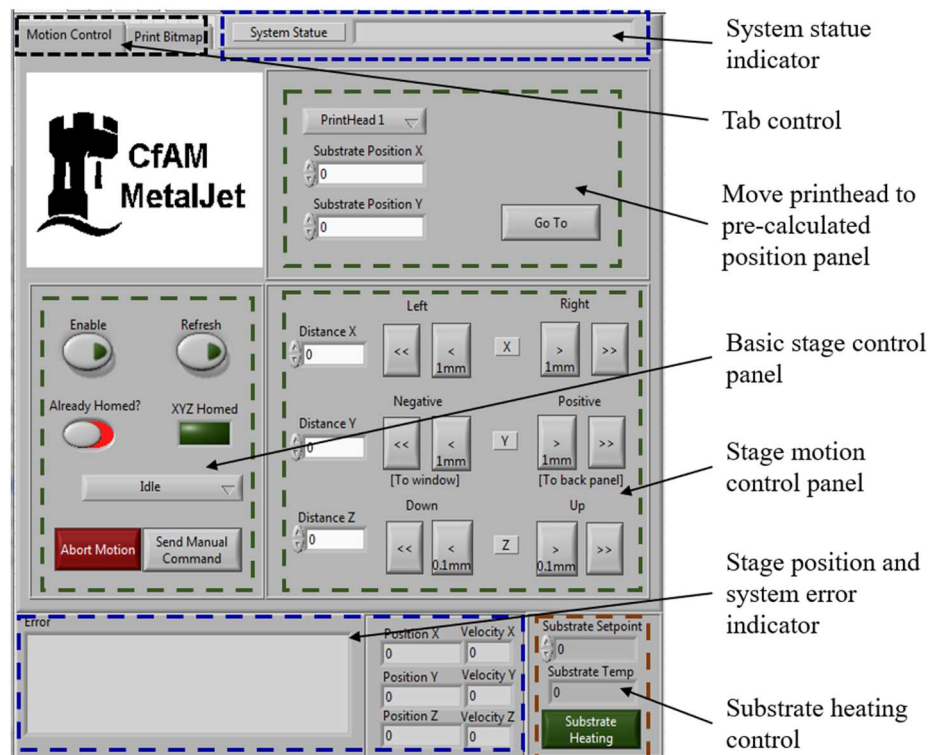


Figure 4.1 User interface of the dual-head MetalJet, main software on “Motion Control” page

The “Print Bitmap” page of the main control VI manages the tuning of jetting and bitmap printing functions, as shown in Figure 4.2. The top blue dashed rectangle is an indicator panel that displays printing progress, for example, “Now printing line 87 layer 2” or “Printing finished”. The blue dashed rectangle below shows the shape and amplitude of the active jetting waveform together with the currently selected printhead. The black dashed rectangle on the left contains the tuning jetting control panel, which allows the operator to adjust current levels and waveform shapes for a given printhead and initiate tuning. The green dashed rectangle at the bottom provides controls for bitmap and calibration printing. In this panel, the operator can set printing parameters such as the bitmap file, number of layers, droplet spacing, and layer thickness. Pre-set printing strategies are also available here.

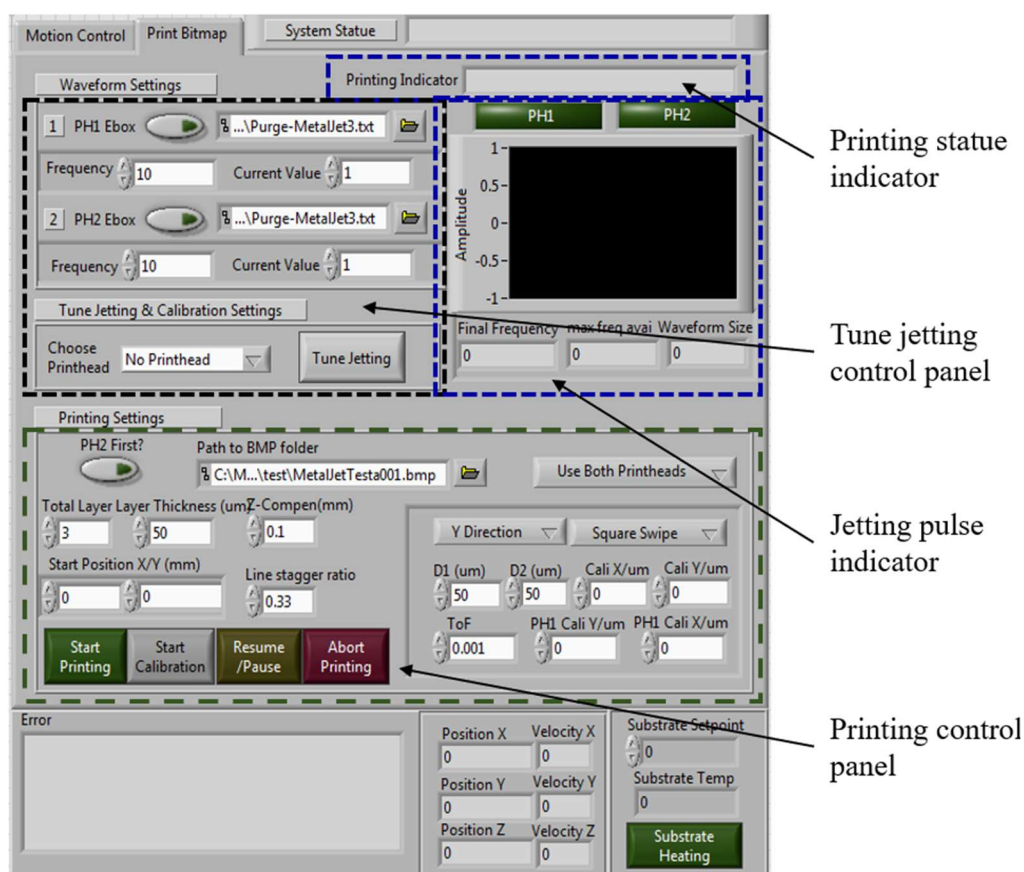


Figure 4.2 User interface of the main software on the “Print Bitmap” page

The user interface for nozzle heating control is shown in Figure 4.3 (a). This interface, implemented as a separate VI from the main program, includes a temperature-time plot, a temperature setting, and heating control functions. It is

separated from the main VI because the induction heater occasionally fails and requires a restart. By isolating this function, other operations can continue unaffected during such interruptions. Figure 4.3 (b) shows the user interface for controlling the LED strobe movement via a stepper motor. This function is also separated from the main VI, as it remains idle for more than 90% of the printing process. Running it as an independent VI allows the operator to close it when not in use, thereby conserving computing resources. On the whole, the user interface is clear and well-structured, and the separation of functions enhances convenience for the operator.

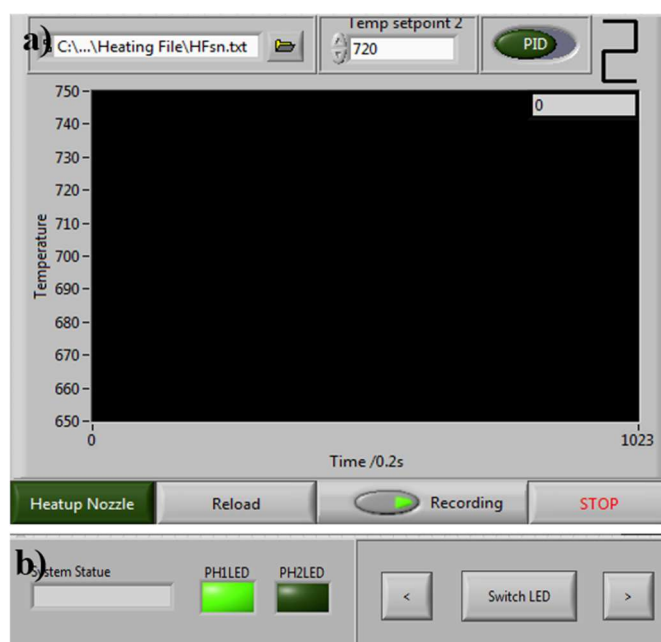


Figure 4.3 User interface of (a) Nozzle heating VI and (b) Strobe LED movement VI

4.1.2 Programming of individual components

A fundamental aspect of developing control software for the dual-head MetalJet system involved clarifying the communication methods between each electronic component and the controlling PC. The primary challenge in programming these components lies in understanding their communication protocols, which are generally governed by serial communication standards. Table 4.2 in the document lists the key devices within the system along with their respective methods of communication. Once the connection interfaces for each device are

established, programming in LabVIEW involves several critical steps: defining the specific port for each device, configuring the port settings, and managing the data transfer.

Table 4.2. Key devices and their serial communication standard

Name of the component	A/D input	A/D output	Serial communication standard	Feedback loop
Substrate Heater	Digital	Analogue	RS 232	Close loop
Motor for LED strobe	Analogue	Analogue	Non-standard DB-9	Open loop
Calibration camera	Digital	Digital	USB	Open loop
Aerotech A3200 Stages	Digital	Digital	C16501-50	Close loop
Waveform Generator	Digital	Digital	GPIO	Open loop
Pyrometer	Digital	Digital	RS485	n/a
Induction Heater	Digital	Analogue	RS485	*Open loop
Relays	Digital	Analogue	Non-standard Digital	Open loop

An example of the LabVIEW control code used for the Aerotech A3200 linear stage is shown in Figure 4.4. This code segment was developed to position the linear stage beneath a designated printhead by moving it to a specified relative location. In LabVIEW, control logic is built using modular virtual instruments (VIs), which can be triggered via the user interface. In this case, the function is executed by a button click. Once activated, the software initiates communication with the linear stage through a “connect” VI, establishing the link between the PC and the motion hardware. The function accepts three user inputs: a printhead selection identifier (referred to as the “*position area*”) and the X and Y coordinates of the desired substrate position. A preliminary check is performed to verify that the input location corresponds to the correct printhead zone. This verification step reduces the risk of operator errors, such as selecting the wrong printhead, and prevents excessive movement that could lead to collision.

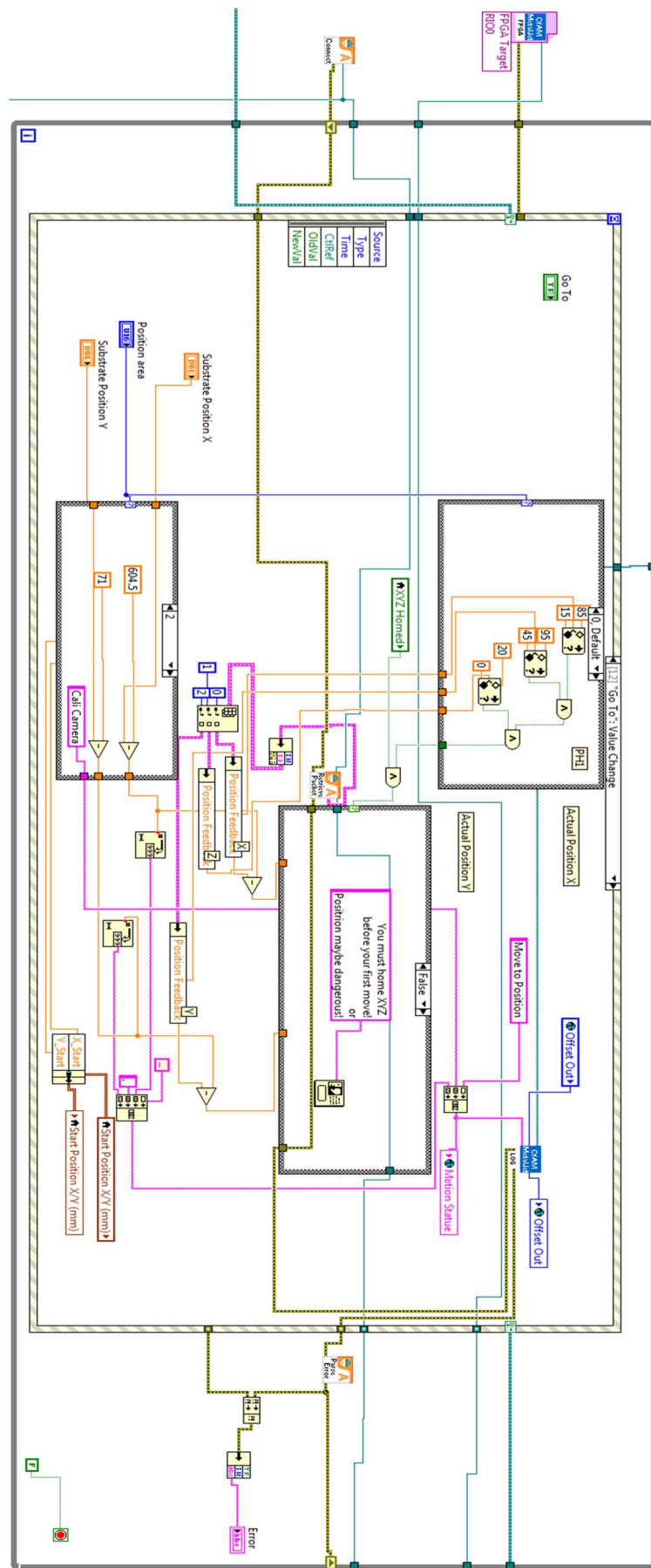


Figure 4.4 Example code of Aerotech A3200 linear stage control

The programme then checks whether the linear stage has been homed. If it has not, the operation is halted and a “not-homed” warning is issued, ensuring positional accuracy before any movement is allowed. If the system passes this check, the movement is carried out using predefined parameters for speed, acceleration, and target position. A “wait” function is incorporated to ensure the motion is completed before any subsequent command is issued. Upon arrival at the target location, the system updates the software interface with the current stage coordinates and system status, confirming that the instruction has been successfully executed. An integrated error-handling routine monitors for faults, logs error codes, and stops stage movement in the event of critical errors. Finally, an “auto-log” VI captures the timestamp, system status, and user actions in a dedicated log file. This file serves as both an experimental record and a resource for troubleshooting. Further details of LabVIEW scripting and implementation practices can be found in Appendix 1: LabVIEW coding for each key device.

4.1.3 Toolpath planning and kinematics

This sub-section introduces the novelty and advancements in toolpath planning software and algorithms of the dual-head MetalJet system. Similar to all the typical inkjet systems, the single-head MetalJet utilises a raster-based toolpath planning approach inherited from traditional Inkjet systems (as mentioned in section 2.5). This method involves the printhead sweeping across the entire toolpath area, depositing droplets as the nozzle reaches predetermined positions. While this technique is effective in Inkjet printing, where multiple nozzles are involved, it proves inefficient in the MetalJet system, which operates with a single nozzle. The inefficiency arises from the considerable amount of time spent traversing non-printing areas, which cannot be offset by multiple nozzles as in Inkjet systems. Furthermore, this legacy toolpath planning lacks flexibility in droplet packing and limits the application of more sophisticated printing strategies.

To address these limitations, the toolpath planning software has been re-engineered. The revised approach is detailed in the flowchart presented in Figure 4.5 (a), with key modifications highlighted in red. The process begins by binarising the bitmap image of the design; however, instead of directly

transferring the binary array line by line, a dual-row integral index array is introduced. This array captures the indices of the first and last non-empty elements on each line of the binary array. By doing so, it allows for the exclusion of empty elements at both the beginning and end of each line. The trimmed line data is then forwarded to the FPGA for accurate mapping and execution. This modification significantly reduces unnecessary movement across empty toolpath areas, as shown in Figure 4.5(b) on the right. The toolpath is now calculated based on the index array, allowing the movement stages to be confined to areas where printing occurs, rather than covering the entire rectangular pattern area. This refined method not only enhances the efficiency of the printing process but also lays a foundational platform for developing advanced printing strategies. By enabling the definition of custom line start points and adjustable row spacing, this new toolpath planning approach facilitates greater control and precision in multi-material MetalJet printing. For the example of the logo pattern shown in Figure 4.5(c), the input bitmap has a size of 260 pixels * 200 pixels. Using a 500 Hz printing frequency, the new toolpath saved 40% time for the first layer and became increasingly efficient in subsequent layers as the required print area decreased.

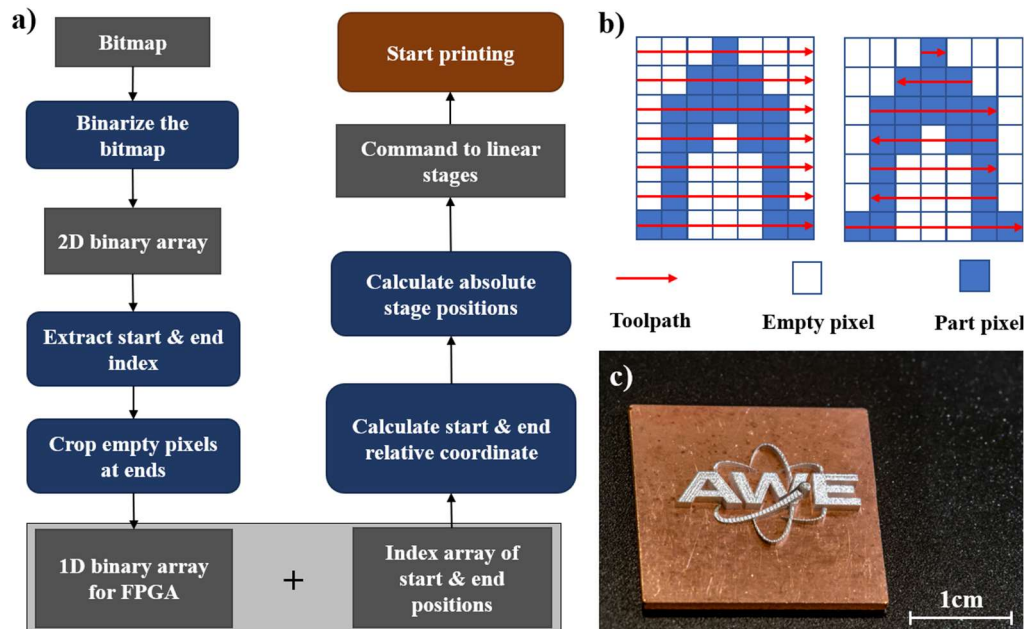


Figure 4.5 (a) Flowchart of the modified toolpath planning method, and diagram of the (b) Original toolpath and (c) Photograph of the sample printed by the new toolpath planning method, which saved over 40% printing time

The toolpath calculation considers the stage acceleration (X_a), stage movement during the droplet flying (X_{tof}) and length to skip (X_b). The printing direction can be either along the X axis or the Y axis. Here, we take printing along the X axis as an example. The total length of the toolpath (X_{tot}):

$$X_{tot} = X_{len} + 2X_a \quad (4.1)$$

where X_{len} stands for the length of the desired printed trace and X_a represents the distance of stage acceleration.

For X_{len} , we define start point index (I_s), end point index (I_e), droplet spacing (ds):

$$X_{len} = ds * (I_e - I_s) \quad (4.2)$$

From the Aerotech A3200 manual book, the acceleration and deceleration curve type and their parameters of the stage are shown in Figure 4.6(a). We define acceleration rate change time as t_j , stable acceleration time as t_a and stable acceleration as ac . The change rate of acceleration (j_c) can be fined as $j_c = ac/t_j$. All these parameters should be synchronised with the actual stage settings. Then we have:

$$X_a = j_c * t_j^3 + \frac{3}{2} * j_c * t_j^2 * t_a + \frac{1}{2} * j_c * t_j * t_a^2 \quad (4.3)$$

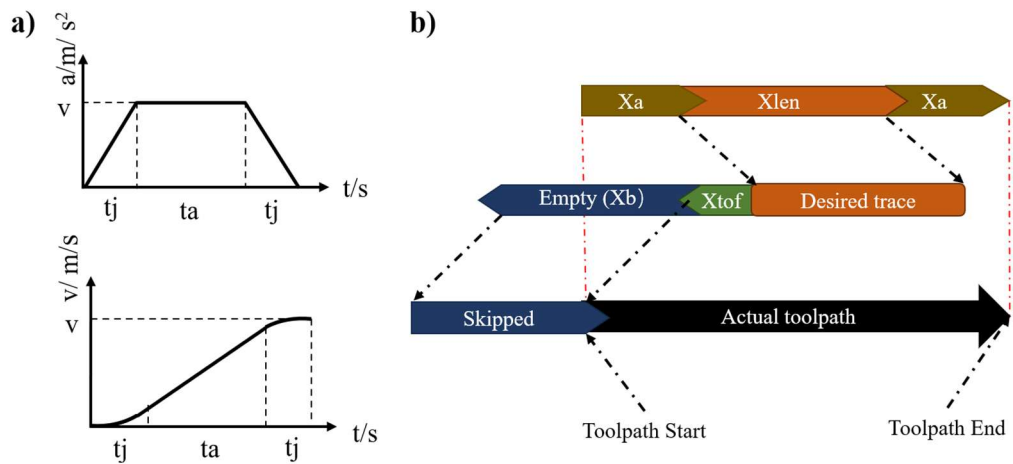


Figure 4.6 (a) Acceleration-time graph and speed-time graph (b) Diagram of the MetalJet toolpath start-end point calculation

During the printing, the printhead is fixed and the building platform keeps moving, the toolpath of the stages counters the actual building direction of the

part. This determines in toolpath start/end point calculations which portion should be set as a minus value. The start point of the toolpath can be defined as:

$$X_{start} = X_a + X_{ph} + X_{rp} - X_{bmp} + X_{cali} - X_{tof} \quad (4.4)$$

Each item in the above equation represents:

X_a : Distance that the stages travelled when reaching the setting speed

X_{ph} : Stage position that points the middle of the building platform to the nozzle

X_{rp} : Relative position of the printed part to the middle of the building platform

X_{bmp} : Empty distance at the beginning of the trace

X_{cali} : Printhead position offset, which is used to align two printheads

X_{tof} : Distance that the stage travelled from the jetting to deposition of one droplet.

Can be define as:

$$X_{tof} = \frac{D}{V_{droplet}} * V_{print} \quad (4.5)$$

where D is the distance between the nozzle to substrate, which is usually set as 1mm. $V_{droplet}$ is the droplet flying speed, which can be read from the strobe camera. V_{print} is the stage speed during the printing, determined as:

$$V_{print} = ds * f \quad (4.6)$$

where f is the jetting frequency and ds is the droplet spacing value.

The end position of the toolpath equals:

$$X_{end} = X_{start} - X_{tot} \quad (4.7)$$

The toolpath start point coordinate perpendicular to the printing direction is:

$$Y_{start} = Y_{ph} - (N_L - 1) \times Y_{pit} \quad (4.8)$$

where Y_{ph} is the Y position of the printhead, N_L is the number of printed lines, and Y_{pit} is the gap between printed lines (usually equal to ds). In addition, due to the introduction of the $[X_{start}, X_{end}]$ array, this software also supports complete

customisation of the starting point, which provides technical support for the subsequent development of the printing strategy.

Incorrect settings of kinematic parameters can lead to systematic and significant printing errors. For example, if the acceleration distance X_a is set shorter than the actual required value, the droplet may be jetted while the stage is still accelerating. This results in increased spacing between the first and second droplets, which becomes more pronounced at high jetting frequencies or with a large nozzle-to-substrate distance. In extreme cases, this can lead to a visible gap, as illustrated in Figure 4.7 (a). Another critical error arises from an incorrect calculation of the total toolpath length, which is often caused by rounding issues in the software. As shown in Figure 4.7 (b), this can cause the final droplet in every two lines to be consistently missing. This occurs when X_{tot} is calculated shorter than what it should be by just a few pitch lengths, causing the stage to stop slightly before the intended droplet trigger point. Such discrepancies are typically introduced when floating-point variables are mistakenly defined as integers, resulting in the truncation of the required distance.

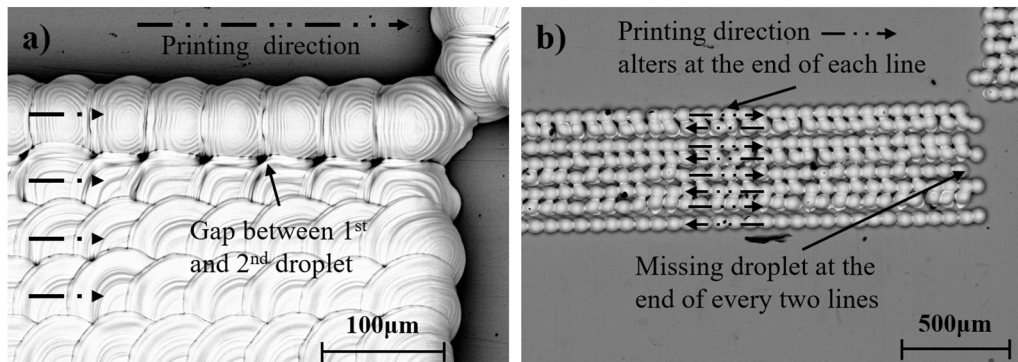


Figure 4.7 Consequences of lack of optimisation of kinematic parameters: (a) SEM image of a sample with a gap between the 1st and 2nd droplet at each line, (b) SEM image of the sample with a regular missing droplet at the boundary

In many single-material AM systems, the placement of patterns is determined based on the absolute coordinate values of the stages, requiring operators to calculate the precise position of each pattern. While this method provides accurate information and is widely adopted in single-printhead and single-

substrate setups, it proved problematic in the more complex dual-head system equipped with four available substrates. The additional complexity significantly increased the likelihood of human error due to the potential for distraction during experiments. One case of human error is shown in Figure 4.8 (a), where the absolute position is wrongly calculated, and a portion of the pattern was printed outside the substrate.

To make the system better fit for multi-material printing tasks, the system utilises relative positioning, which simplifies the operator's tasks and reduces the scope for errors. As illustrated in Figure 4.8(a), the system calculates the pattern's position relative to the centre of the substrate. This involves dividing the absolute position into two components: a “checkpoint” position, which is established when the printhead is aligned with the centre of the substrate, and a relative position that specifies the pattern's location on the substrate. In this case, the toolpath is defined relative to the setpoint of the pattern position. This approach, particularly beneficial in a research setting, enhances operational clarity by directly linking pattern placement to a fixed reference point, thus making the process more intuitive.

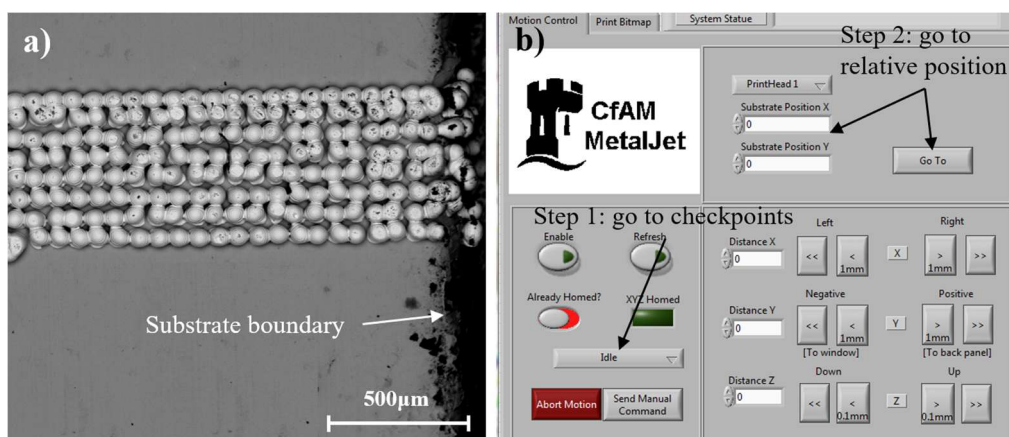


Figure 4.8 (a) SEM image of a sample printed wrongly calculated location by the operator (b) “Checkpoint + relative” positioning method to define the position of a pattern

Additionally, an assistance software has been introduced to improve visibility and clarity regarding what has already been printed on the substrate, as displayed in Figure 4.8(b). Due to the proximity of the substrate to the printhead and the spatial constraints within the printer, it is challenging to visually confirm

the nozzle's position or to use a camera close to the nozzle because of the high temperatures and limited space.

To overcome these visibility issues, a simple assistance software has been developed. The user interface is shown in Figure 4.9. This software visually represents the expected printings on the substrate, assisting the operator in organising the prints effectively. It helps prevent potential overlaps and ensures that all prints are correctly positioned on the substrate, thereby optimising the printing process and enhancing the overall usability of the MetalJet system.

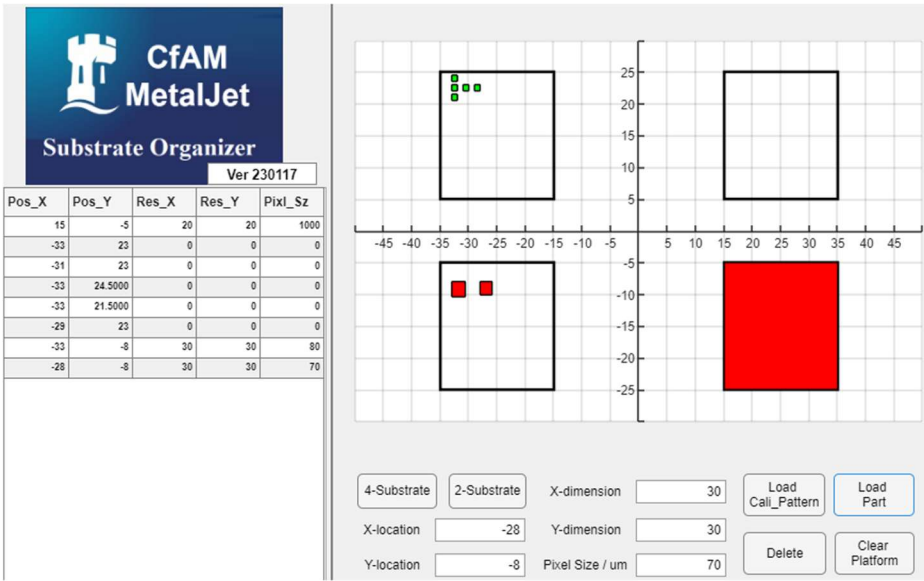


Figure 4.9 User interface of the assistance software “Substrate Organiser”

4.1.4 Printhead alignment algorithm software design

Achieving precise alignment of the two printheads is crucial for ensuring the quality of multi-material MetalJet printing. The alignment calibration function has been enhanced by incorporating an improved algorithm that takes into account the angle between the printhead axis and the camera lens, addressing issues in the original alignment methods. The calibration process begins with the use of a CCD camera to capture an image of two 6x6 droplet arrays printed by each printhead, as outlined in the flowchart displayed in Figure 4.10(a). The captured image is shown in Figure 4.10(b). Initially, the camera captures the image, and an ROI is selected through the software. The primary challenge is

identifying the droplets within the image accurately, as droplets often do not appear perfectly circular due to imaging discrepancies.

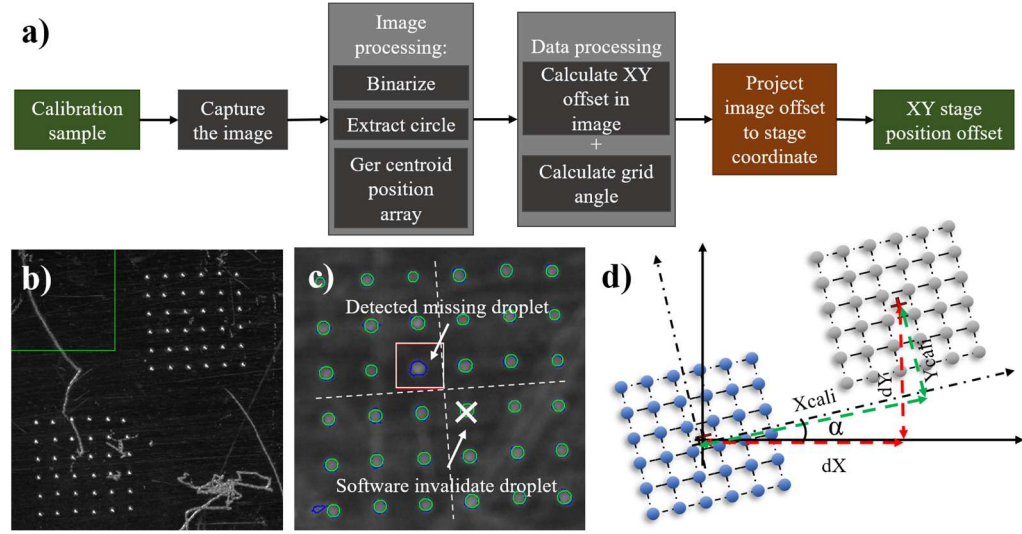


Figure 4.10 (a) Flowchart of calibration process (b) Camera image of captured calibration droplets array (c) Camera image of droplet boundaries (green circle) detected by the calibration software, detected missing droplet marked in white rectangle, and software invalidates droplet marked with a white cross (d) Diagram of the influence of angle between camera coordinate and linear stage coordinate

Instead of relying on a circular Hough transform, which can lead to significant errors due to its assumption of perfect circularity, the upgraded software employs a polygon-based matching algorithm. This approach involves reading the detected region as a polygon and assessing its shape based on roundness and the dimensions of its major and minor axes to confirm if it indeed represents a droplet. This step necessitates the binarisation of the image within the ROI and the extraction of its boundary. Users must adjust the image's brightness and contrast settings to ensure optimal droplet detection.

Following droplet recognition, the algorithm proceeds to ascertain the position of the printhead based on the droplet array, which appears as a grid in the image. The centroids of the extracted shapes are calculated, as shown in Figure 4.10(c), and the position of a specific droplet is denoted as $C_{ab}(X_{(a,b)}, Y_{(a,b)})$, where a and b represent the row and column numbers of the droplet, respectively. The grid's coordinate position is determined by averaging these centroid coordinates. If

any droplet fails to be detected, its coordinates and those of its symmetrical counterpart are invalidated (set to zero), ensuring accuracy in grid positioning. For example, when the droplet in row 3 column 3 is detected missing, as shown in the white rectangle in Figure 4.10 (c), the symmetrical counterpart of it is a detected droplet in row 4 column 4, which will be invalidated by the software. Then the coordinate position of the grid (X_{grid} , Y_{grid}) can be defined as:

$$X_{grid} = \frac{\sum_{(1,1)}^{(6,6)} X_{(a,b)}}{36 - 2 * n} \quad (4.9 - 1)$$

$$Y_{grid} = \frac{\sum_{(1,1)}^{(6,6)} Y_{(a,b)}}{36 - 2 * n} \quad (4.9 - 2)$$

Where n is the number of droplets that were not detected by the software.

The algorithm of offset relies on the offset between the two printheads in the camera image, shown as d_X and d_Y . However, the actual experiment always sees a 3-5um gap or overlap in the printing. This is due to the angle α between the printing direction and the camera, as shown in Figure 4.10(d). When taking α into consideration, the offset calculation changed to:

$$CaliX = d_X \times \cos \alpha - d_Y \times \sin \alpha \quad (4.10 - 1)$$

$$CaliY = d_Y \times \cos \alpha + d_X \times \sin \alpha \quad (4.10 - 2)$$

The alignment error comes from three places, which will be discussed below: slicing, alignment method and alignment position.

The slicing error E_{slice} indicates the error brought by slicing. An example of a slicing error is shown in Figure 4.11 (a), where the tiny difference at the boundary is caused by slicing rounding. For any given part, its physical dimensions rarely correspond exactly to an integer multiple of the droplet diameter. As a result, the slicing algorithm must accept a degree of dimensional error when converting the original geometry into a discrete droplet-based raster or toolpath. As demonstrated in Figure 4.11 (b), the maximum slicing error $E_{slice_{max}}$ is half of the droplet diameter, which can be referred to as:

$$E_{slice_{max}} = \frac{1}{2} * ds \quad (4.11)$$

where ds means the droplet spacing. In the case of MetalJet, where pixel size is around $50\mu\text{m}$, the maximum E_{slice} is $20\mu\text{m}$.

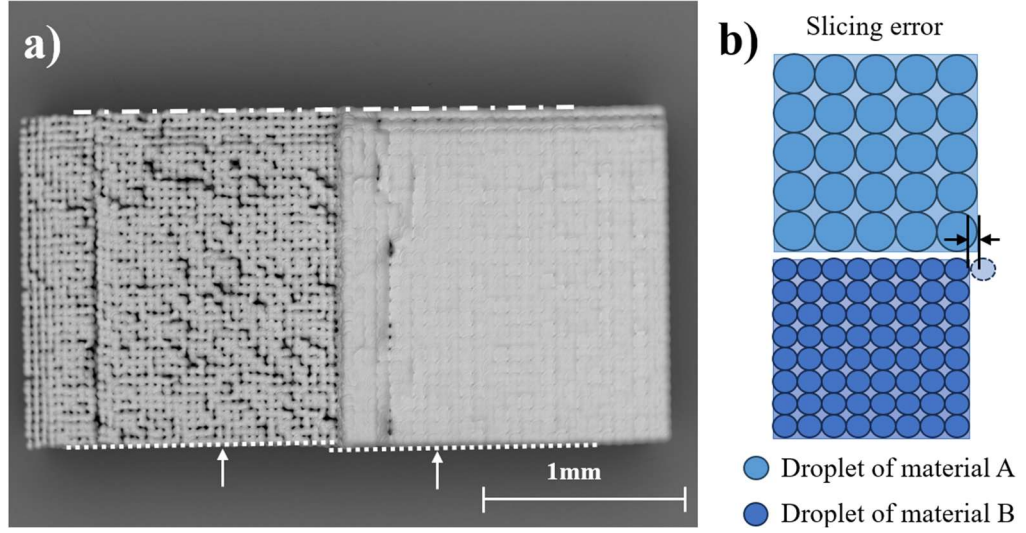


Figure 4.11 (a) SEM image of a Sn-In multi-material sample with an unaligned boundary due to slicing error (b) Diagram of slicing error

The alignment method is whether the software aligns the pattern on its boundary or its pixel. An example of this kind of alignment error is shown in Figure 4.12 (a). These two alignment methods will bring significant differences when the diameter of the droplets of two materials becomes large, as shown in Figure 4.12 (b), which is called E_{mtd} . Maximum error caused by alignment position ($E_{mtd\ max}$ is the radius difference of the droplets from two materials, which can be referred to as:

$$E_{mtd\ max} = \frac{1}{2} * |ds2 - ds1| \quad (4.12)$$

The alignment position indicates the point in the pattern that is used for alignment. This error E_{pst} from root also comes from the dimension difference during the slicing, which can be regarded as a method of distributing slicing error E_{slice} . Taking the checkerboard pattern as an example, the slicing error is lower when aligning at the pattern centre instead of the pattern corner. The diagram in Figure 4.13 (a) shows the difference between these two methods. However, the optimal alignment position highly depends on the design of the pattern and the accuracy requirement of the part. In this case, E_{pst} cannot be presented by an equation. However, aligning at the centre of the pattern is

usually a good choice. Figure 4.13 (b) shows an example of alignment at the centre of the pattern where errors are evenly distributed.

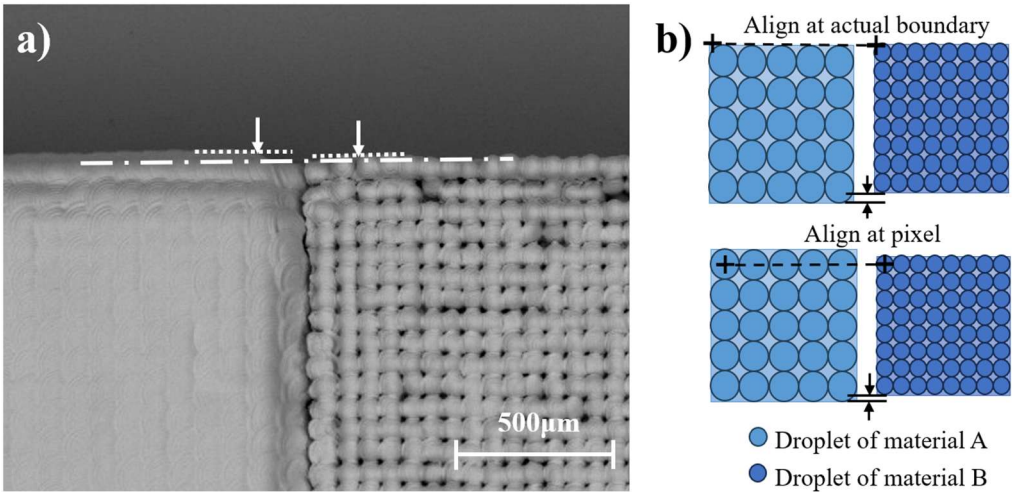


Figure 4.12 (a) SEM image of a Sn-In multi-material sample with a gap due to aligning at the boundary (b) Diagram of the error difference in aligning at the boundary and pixel

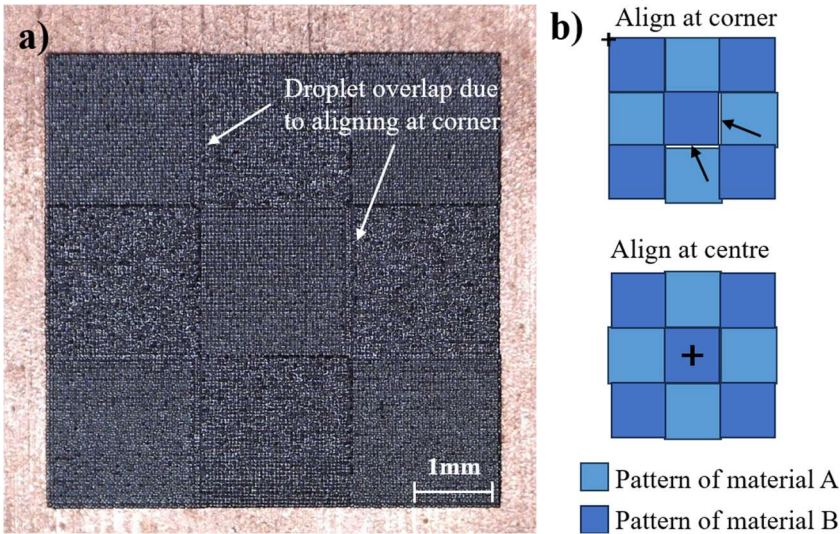


Figure 4.13 Camera image and diagram of a Sn sample fabricated with two printheads with droplets overlapped due to aligning at the pattern corner instead of at the pattern centre

4.2 System evaluation

The dual-head MetalJet system underwent evaluation through a series of initialising tests using Sn and Ag to represent materials with low and high melting points, respectively. However, the initial experiments encountered several hardware issues, necessitating a detailed process of system troubleshooting. This section is divided into two parts: the first addresses the resolution of these hardware failures, and the second presents the outcomes of the successful initialising tests.

4.2.1 System troubleshooting

The system troubleshooting section focuses on finding out the cause of the issues during the printing process and finding a reliable solution. The issues include failure in digital temperature reading, failure in the high-frequency generator and printing pattern “drifts”.

4.2.1.1 Bypass the digital temperature reading

A significant hardware issue encountered during system evaluation was the loss of temperature readings from both pyrometers. This problem was traced to an abnormally low output signal voltage between pin 2 and pin 3 on the RS232 port of the PC, which is a National Instrument device equipped with a built-in data acquisition module. The diagram of the connection is shown in Figure 4.14(a). Resolving this issue by sending the module to National Instrument for repairs was estimated to take between 6 to 9 months.

To circumvent this lengthy downtime, an alternative solution was identified in the pyrometer’s manual, which indicated the presence of an analogue output, as illustrated in Figure 4.14(b). A bypass strategy was implemented by connecting the analogue output from the pyrometer directly to an FPGA extension module capable of reading analogue signals. Subsequently, the PC would read these signals from the FPGA module and convert them into actual temperature readings. The schematic of this bypass setup is shown in Figure 4.14(c). This new method restored temperature monitoring functionality with the same level of accuracy as the original digital signal method. The primary difference noted was that the analogue signals, being raw data without any inherent digital or

analogue filtering, displayed greater fluctuations compared to the digital method. To address this variability, digital filtering techniques were applied within the LabVIEW programming environment. Specifically, averaging five consecutive readings provided a more stable and reliable temperature value, effectively mitigating the impact of the fluctuations and ensuring the continuation of precise temperature monitoring within the system.

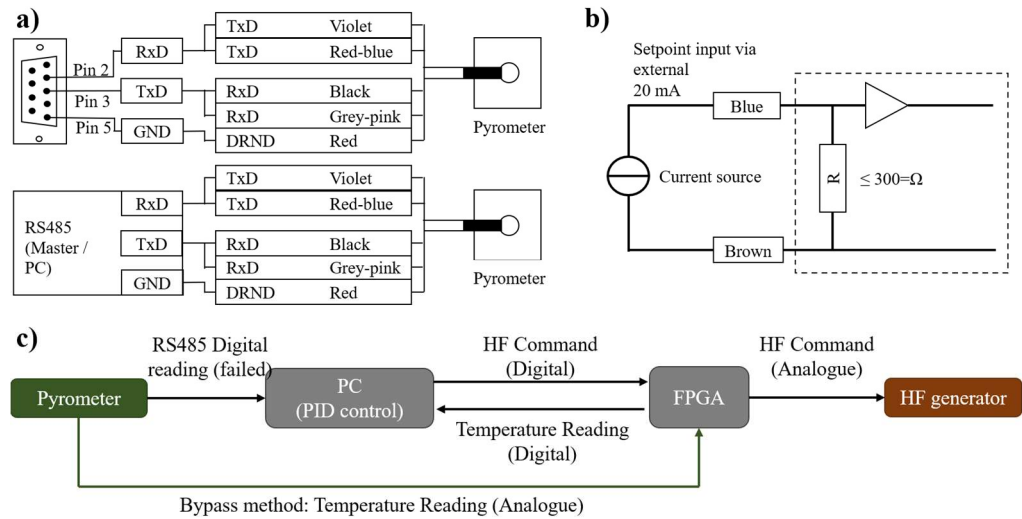


Figure 4.14. (a) RS232 connection to the pyrometers, (b) Analogue reading connections to the pyrometers, (c) diagram of the bypass solution.

4.2.1.2 High-frequency generator failure

During a routine experiment, the induction heating process was abruptly halted, displaying an error message "Fault Frequency Low" on the system's interface, as illustrated in Figure 4.15(a). The initial step in addressing this issue involved a detailed examination of the mechatronic connections within the cartridge heating loop, which is depicted separately for clarity in Figure 4.15(b).

The troubleshooting procedure commenced with a review of the potential causes for this error, as outlined in the Himmel manual. The error could be triggered by several factors:

1. Excessive load being heated.
2. Insufficient input voltage to the induction heater.
3. Overly high output demand.
4. An internal device malfunction.

To diagnose the problem, measurements were first taken of the power supply level and the magnitude of the analogue signal. Both inputs were found to be within normal ranges, suggesting that the issue did not stem from the initial two potential causes. Subsequently, the cartridge being heated was replaced to eliminate the possibility of an overload issue; however, the fault persisted. Given the elimination of other potential causes, the focus shifted to the likelihood of an internal fault within the device. To test this hypothesis, a spare high-frequency generator was installed. Upon replacement, the error ceased, confirming that the original generator had likely succumbed to age-related deterioration.

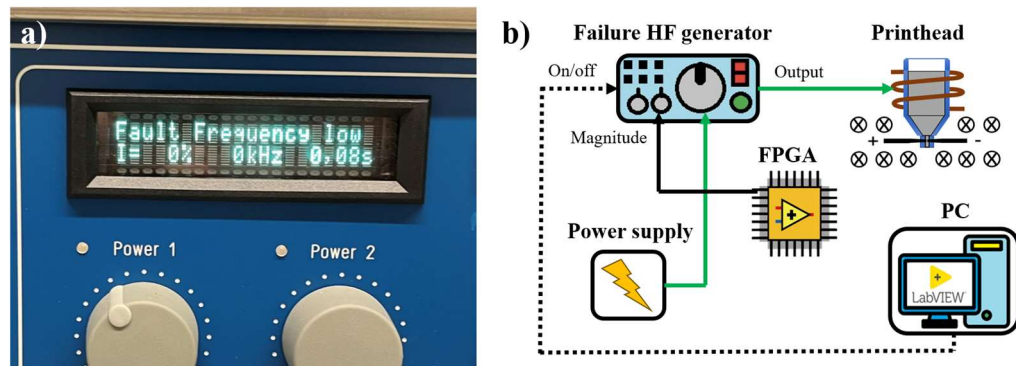


Figure 4.15. (a) Failure of the HF generator and error message (b) diagram for HF generator troubleshooting

4.2.1.3 Solving the printing “drift” issue

During the initial phase of MetalJet printing experiments, an issue was encountered where printouts from the same printhead would not align with its previous outputs over time, exhibiting a random displacement sometimes as large as 100 μm . This phenomenon, termed "drift", is depicted in Figure 4.16(a) and raises concerns about the precision and reliability of the printing process.

Potential Causes of Drift:

1. Thermal expansion of mechanical parts, including cartridge fittings, printhead, and substrate.
2. Variations in jetting trajectory.
3. Mechanical movement of the substrate due to stage acceleration and deceleration.

To systematically address and diagnose the root causes of drift, a structured experiment plan was devised. This involved three groups of printings, where each group consisted of six scattered patterns ($ds = 120 \mu\text{m}$), printed with a 15-minute interval between them to allow any slow-acting changes to manifest clearly. During these intervals, the strobe camera recorded the jetting trajectory for each pattern. The specific experimental conditions were:

1. The building platform remained close to the printhead during idle times without switching between printheads.
2. The building platform was positioned away from the printhead vertically during idle times, without switching between printheads.
3. The building platform was kept away from the printhead vertically and switched between the printheads five times during the idle period.

From the outcomes of groups 1 and 2, the effects of thermal expansion were assessed, while the comparison between groups 2 and 3 helped exclude the impact of mechanical movement. By analysing the patterns and corresponding trajectory records within each group, the influence of trajectory changes was evaluated.

As revealed in Figure 4.16(b), only one instance of drift was observed during the six-hour experiment, occurring in the third pattern of group 2. This isolated occurrence suggested that the drift was primarily induced by changes in the trajectory. However, the displacement exceeded $120\mu\text{m}$, which is significantly more than what a 2° trajectory change would typically cause. Given a standard nozzle-substrate spacing of 1mm , a 2° trajectory change should result in a displacement of approximately $34\mu\text{m}$, d_1 calculated as:

$$d_1 = 1000 * \tan 2^\circ = 34 \mu\text{m} \quad (4.13)$$

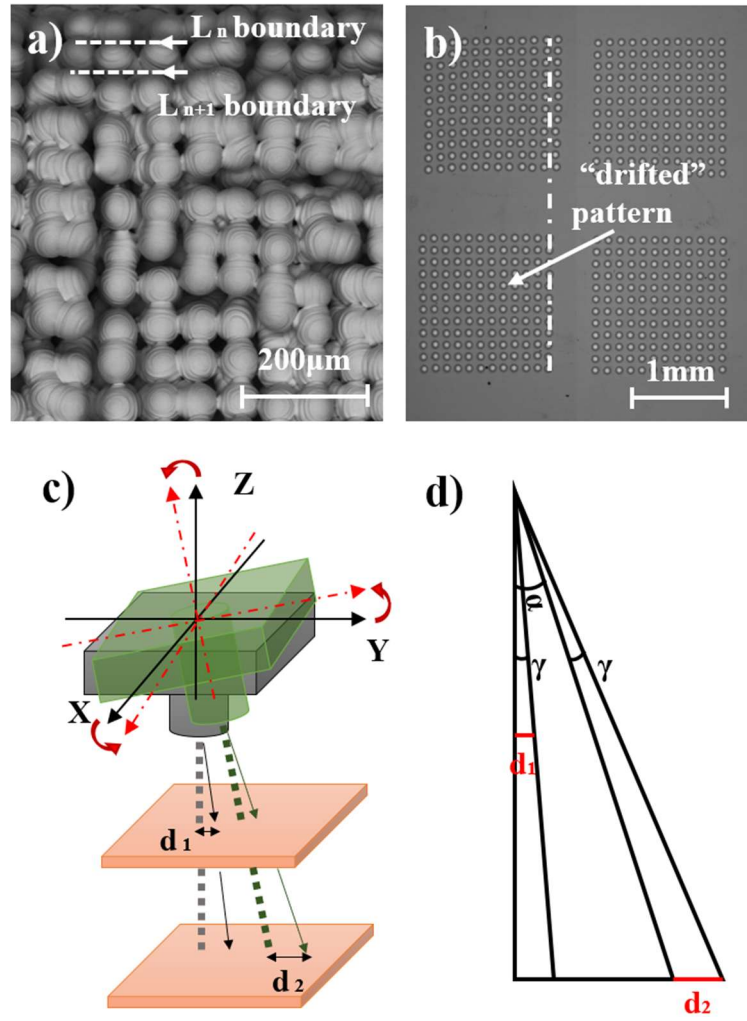


Figure 4.16 (a) SEM image of a Sn sample with misaligned interlayer boundaries due to the “drift” problem (b) SEM image of a series of patterns showing the “drift” pattern in the troubleshooting experiment (c) diagram showing how the trajectory’s influence is magnified

Further investigation revealed that the printheads had been inadvertently elevated by an additional 1.5mm and 2mm, resulting in increased spacing of 2.5mm and 3mm, respectively. Additionally, both printheads exhibited a tilting along the Y-axis of 10° and 16°, amplifying the error d_2 from trajectory changes as follows:

$$d_2 = 3000 * [\tan(\alpha + 2^\circ) - \tan \alpha] = 90 \sim 114 \mu m \quad (4.14)$$

when α is 16°. These mechanical adjustments likely occurred during installation and, once corrected, have not recurred.

This troubleshooting highlighted that even small deviations in trajectory, such as a 2° variation, could cause noticeable displacement in printing. This becomes particularly problematic in dual-head printing, where even minor misalignments can result in significant gaps or overlaps. The insights from this issue underscore the critical need for precise alignment and consistent jetting in multi-material MetalJet processes, frequent alignment calibrations, and strict maintenance of the nozzle-to-building plane distance to ensure high-quality printing outcomes. Several later printing samples verified this speculation, one of which is shown in Figure 4.17.

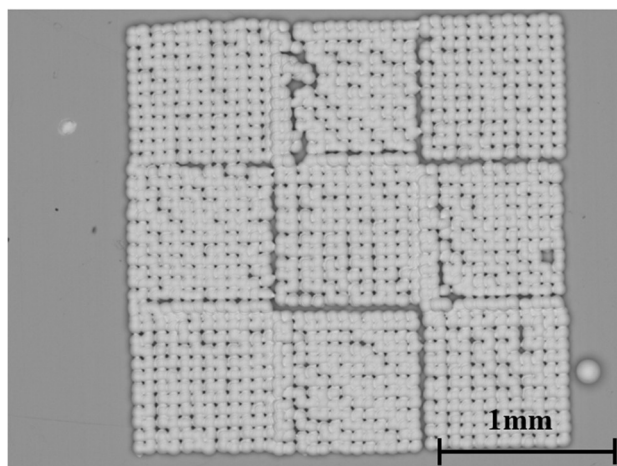


Figure 4.17 SEM image of a Sn sample fabricated by two printheads with gaps due to the alignment error of $15\mu\text{m}$.

4.2.1.4 Other printing failure troubleshooting

The process of system development and evaluation also involves addressing various printing failures that can significantly impact the quality of the output. The following are key issues identified and analysed:

1. Satellite

SEM imagery, as seen in Figure 4.19(a), captures the effect of satellite droplets during jetting, which scatter small particles randomly across the sample. This phenomenon leads to a disordered arrangement of printed droplets, stemming from the unstable jetting process induced by these satellites.

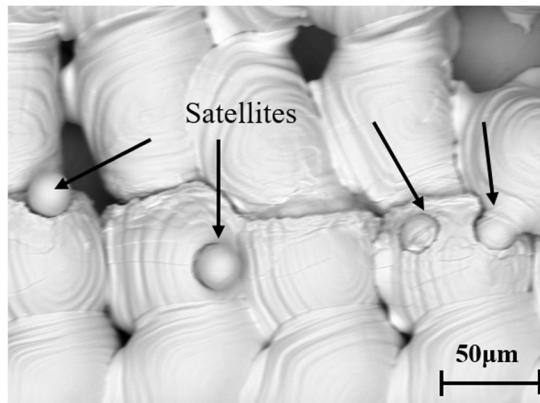


Figure 4.18 SEM image of a Sn sample with satellites

2. Unstable jetting

Figure 4.19 (a) and (b) depict sample defects due to unstable jetting. The reason of unstable jetting can be factors such as clogging at the nozzle, asymmetrical coating at the orifice, or issues related to wetting. The severity of jet instability varies; mild instability might result in local voids or droplet stacking, such as the gaps within 5µm highlighted in the circle in Figure 4.19 (a), whereas more severe instability can lead to random droplet deposition, as shown in Figure 4.19 (b).

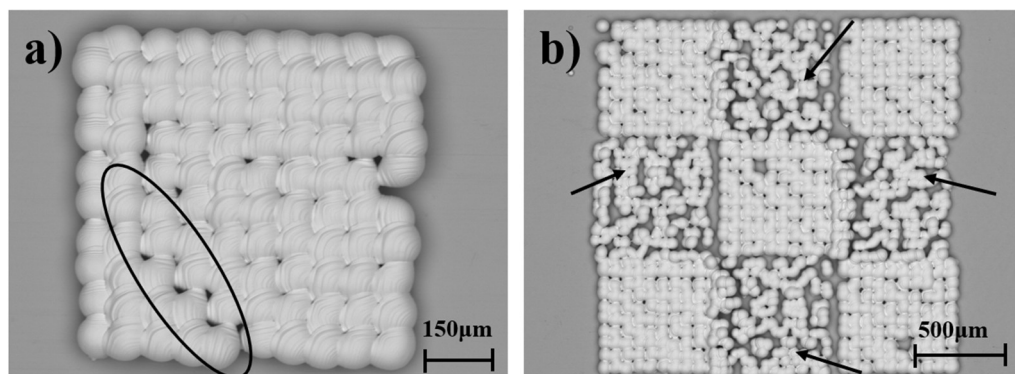


Figure 4.19 (a) SEM image of a Sn sample with gaps due to unstable jetting, (b) SEM image of a Sn sample fabricated by 2 printheads, with one printhead showing a random deposition due to unstable jetting.

3. Sub-optimised droplet spacing

Incorrect droplet spacing can also detrimentally affect print quality. Figure 4.20 (a) illustrates the problem of “droplet stair-up” caused by applying droplet spacing 8µm smaller than the optimal value, while Figure 4.19(b) shows

significant porosity resulting from applying droplet spacing $5\mu\text{m}$ bigger than the optimal value. Droplet spacing calculations are dependent on accurate droplet diameter readings, suggesting that issues such as an unfocused camera can indirectly contribute to these problems.

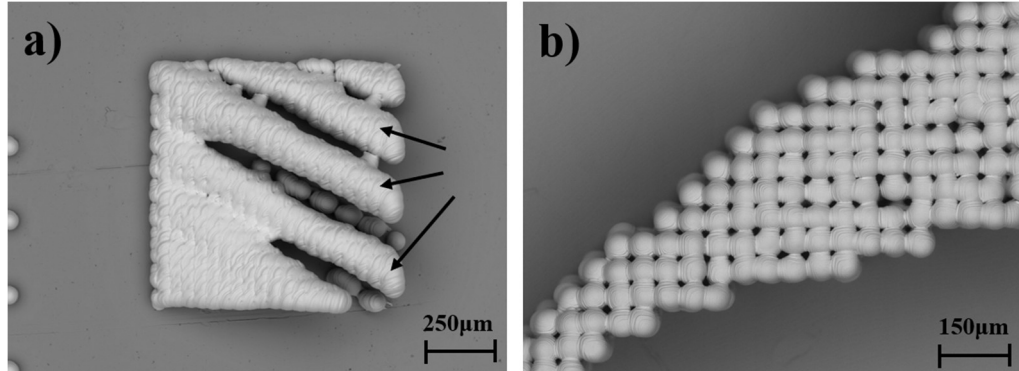


Figure 4.20 (a) SEM image of a Sn sample with staring up droplets due to the applied droplet spacing being $8\mu\text{m}$ smaller than the optimal value (b) SEM image of a Sn sample with gaps between droplets due to the applied droplet spacing being $5\mu\text{m}$ bigger than the optimal value.

4. Missing droplet

Figure 4.21 demonstrates a failure characterised by missing droplets. Upon investigation, it was determined that this was due to occasional non-responsiveness of the FPGA. Given the random occurrence and low frequency of this issue, coupled with the fact that subsequent layers generally cover up these defects, and considering the high costs and extensive time required to replace the FPGA, there is currently no plan to rectify this issue.

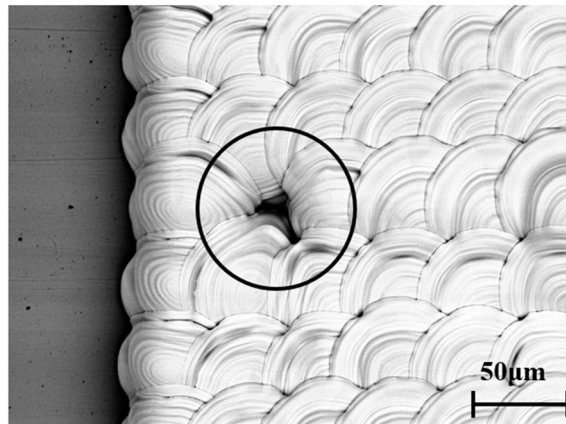


Figure 4.21 SEM image of a Sn sample with a missing droplet

4.2.2 Initialising test

4.2.2.1 Sn initialise printing results

The initialising tests for Sn printing began with an important assessment of the phase-changing temperature, which was accurately measured at 220°C. This temperature is close to the melting point of Sn, which is 231°C, confirming that the bypassed temperature reading from the analogue signal was effectively within an acceptable range for low-temperature operations.

During the experiment, the cartridge temperature was gradually increased to 680°C, as depicted in Figure 4.22(a). This nozzle temperature is chosen because the high-temperature pyrometer installed on the second printhead has a reading range of 650°C to 1500°C. Upon reaching the target temperature, the PID temperature control program efficiently took charge, stabilising the cartridge temperature using the high-frequency generator. This seamless transition highlighted the effectiveness and responsiveness of the PID control system in maintaining the desired temperature settings.

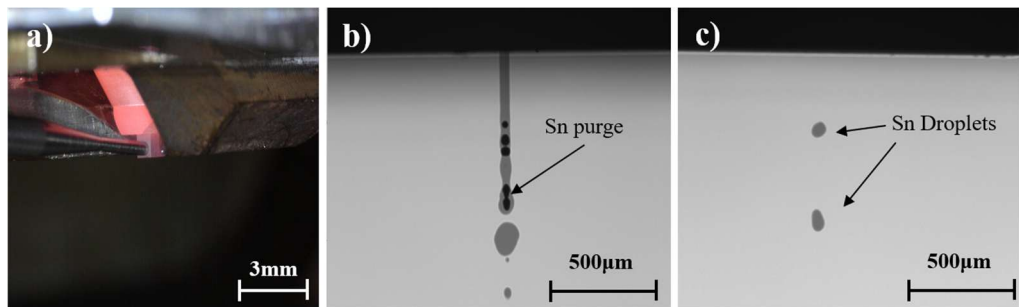


Figure 4.22 (a) Glowing cartridge while heating up during an Sn jetting experiment (b) Stroboscopic image of Sn purge (c) Stroboscopic image of Sn droplets

A critical step in initialising the nozzle involved performing a purge, which is crucial for ensuring that the nozzle functions correctly. As illustrated in Figure 4.22(b), the purge was executed flawlessly, producing a straight, stable, and extended stream, which indicates an optimal nozzle condition. Subsequently, the purge pulse was switched to a 10Hz jetting pulse with an amplitude of 60A. Adjustments were made to the amplitude to achieve a droplet flying speed of approximately 1m/s, and the droplet size was consistently measured at 54µm

with a perfectly vertical trajectory of 90° . These outcomes demonstrated that both the pulse generation system and the jetting observation system were operating effectively.

Following the calibration of the pulse amplitude, a series of test patterns was executed to further validate the printing capabilities. The initial test pattern, a 3x3 checkerboard, consisted of 20 droplets in both length and width per grid, with a single layer thickness, as shown in Figure 4.23 (a). The surface quality of the sample was subsequently examined using SEM, with the results displayed in Figure 4.23 (b).

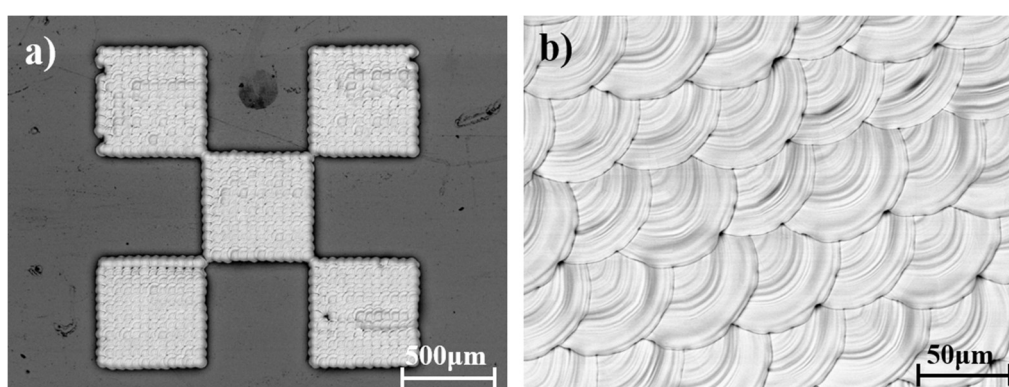


Figure 4.23 SEM image of a Sn checkerboard pattern

Further tests included printing an electric circuit and a heat sink; the latter was separately printed, removed from the substrate, and then positioned onto the circuit. The finest feature within the circuit measured two droplets in width, with all features accurately rendered as visible in Figure 4.25.

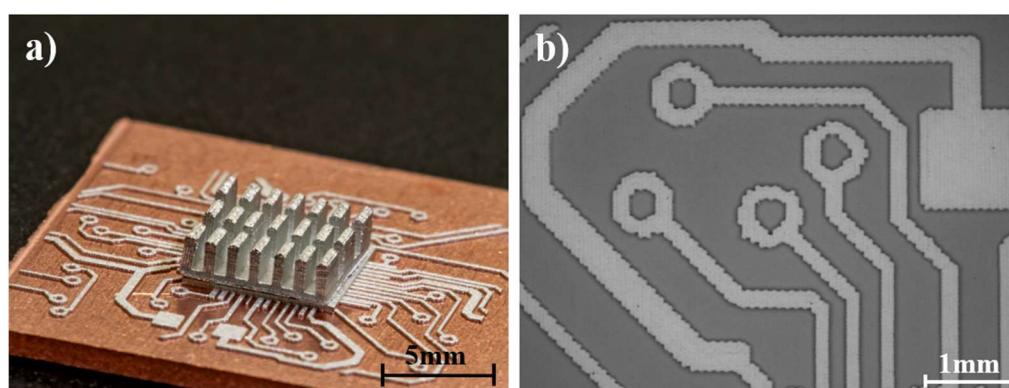


Figure 4.24 (a) Photograph of a printed Sn circuit with Sn heat exchanger (b) SEM image of part of the printed circuit

The final sample produced was a printed QR code, which successfully directed to the CfAM website when scanned, as evidenced in Figure 4.25.

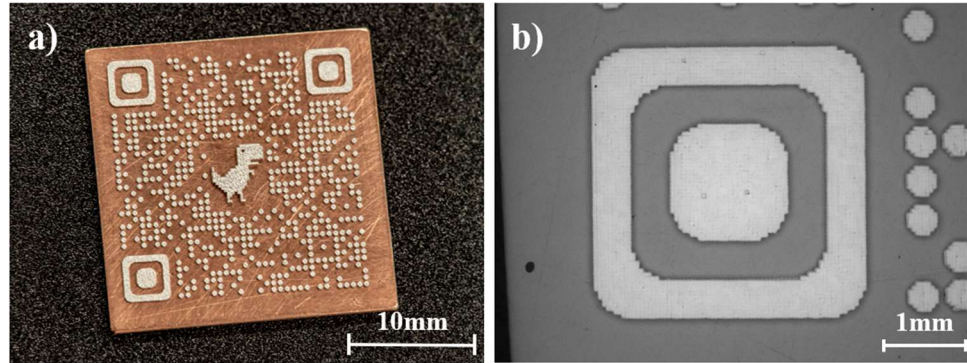


Figure 4.25 (a) Photograph of the printed Sn QR code (b) SEM image of the upper-left corner of the QR code made of Sn

4.2.2.2 Ag initialise printing results

The melting point of Ag is 961.8°C . During the tests, the phase-change temperature was observed at approximately 1000°C , slightly higher than the expected value due to a 40°C error attributed to the pyrometer's reading inaccuracy. Consequently, the nozzle temperature was recorded at 1050°C , though the actual temperature was estimated to be closer to 1000°C .

The initialisation phase commenced with sending a 10Hz purge pulse at a current level of 90A to the electrodes. The resulting purge, as depicted in Figure 4.26 (a), demonstrated a clean and defect-free shape, confirming the operational efficacy of the cartridge. Subsequently, a 10Hz jetting pulse at 60A was applied to the electrode, which was promptly adjusted to 62A to achieve a droplet flying speed of 1m/s. The droplet diameter, as captured by the JetXpert camera, was measured at $70\mu\text{m}$, as shown in Figure 4.26 (b).

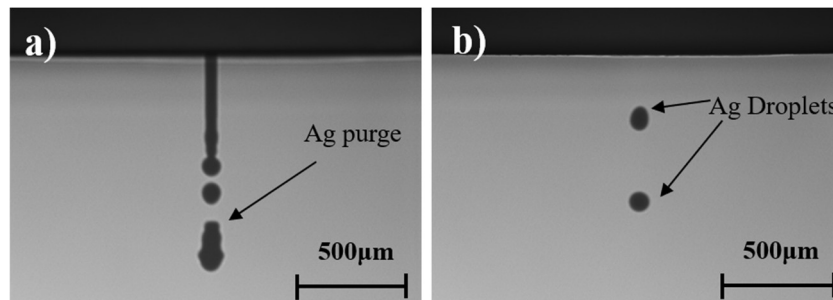


Figure 4.26 Stroboscopic images of (a) Ag purge (b) Ag droplets

Following the successful jetting setup, a checkerboard pattern was printed at a frequency of 100Hz, with droplet spacing finely tuned to 60 μm . Each cell within the checkerboard consisted of 20 droplets in both width and length. The surface morphology of the printed Ag checkerboard pattern is shown in Figure 4.27 (a), with a magnified view of one cell presented in Figure 4.27 (b). The droplets were precisely arranged without significant misplacement, although some porosity was observed among the droplets. Given the limitations in reducing droplet spacing further, this degree of porosity was deemed minimal. A close-up of a single droplet within the pattern is displayed in Figure 4.27 (c), aligning with previous MetalJet Ag printing results referenced in the literature [45].

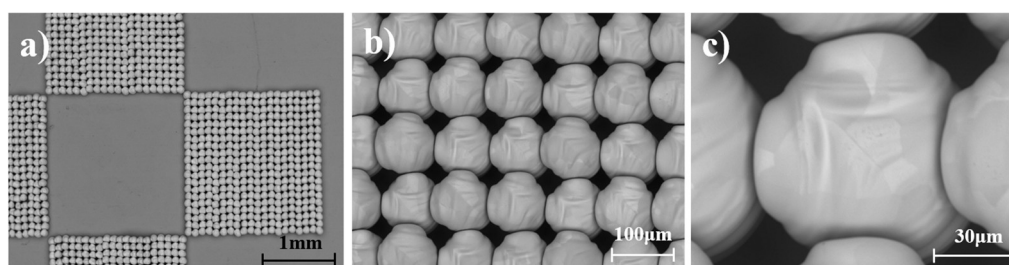


Figure 4.27 (a) SEM image of Ag checkerboard pattern (b) SEM image of the top layer of Ag droplet (c) SEM image of one Ag droplet with surrounding droplets

4.2.2.3 Printhead alignment Results

Following the resolution of the "drift" issue outlined in the troubleshooting section, a printhead alignment experiment was successfully conducted. The test involved fabricating a 3x3 checkerboard pattern using two printheads with tin (Sn). The stability of the jetting from cartridge PH2 was suboptimal, leading to sporadic errors in droplet displacement and resulting in a coarse surface texture of the printed pattern. Despite this, the defect was deliberately retained to make the distinctions between patterns produced by different printheads more discernible. Figure 4.28 (a) to (d) displays images of the 1-layer checkerboard pattern specifically designed for assessing printhead alignment. The observed gaps and overlaps in the pattern were determined to be within a 10 μm error margin. This level of accuracy is considered acceptable given two complicating factors: the variance in droplet size between the two nozzles and the jetting

inconsistencies from PH2, which contributed to displacement errors in the printed patterns.

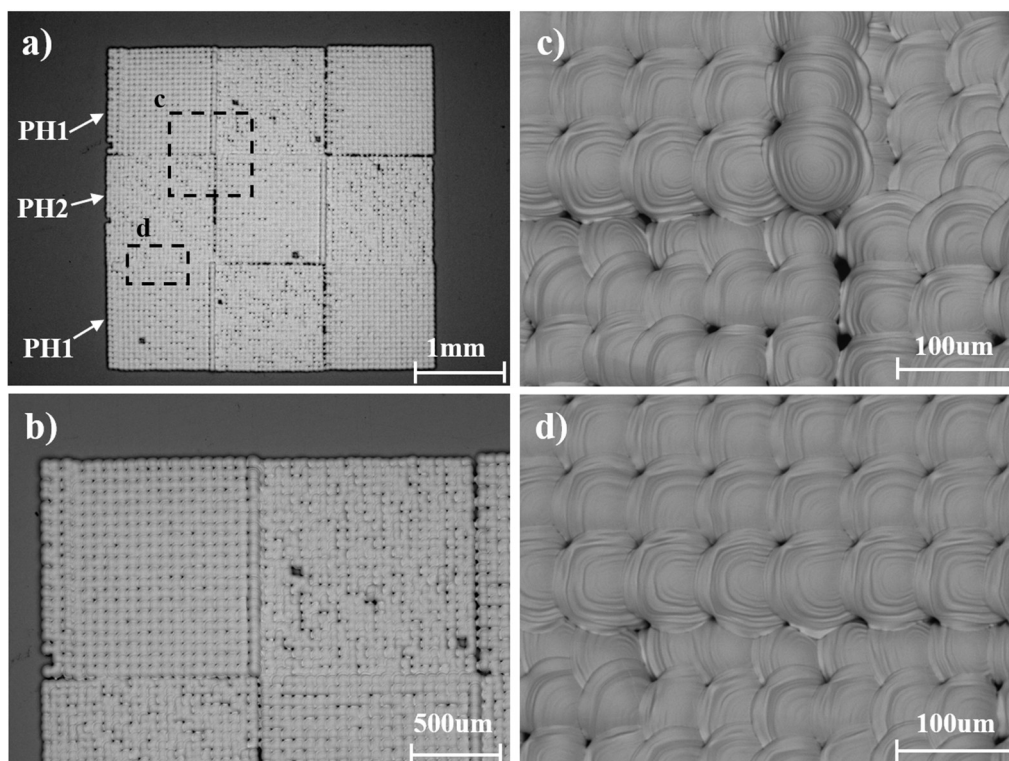


Figure 4.28 SEM images of the 1-layer checkerboard pattern printed with both printheads using Sn

Subsequently, a more complex 5-layer checkerboard pattern was constructed, as shown in Figure 4.29, which demonstrated an improved alignment error within $7\mu\text{m}$. This pattern also employed one cartridge with consistent jetting and another with less stable jetting to further delineate the outputs from different printheads. The successful fabrication of these checkerboard patterns not only highlights the effectiveness of the refined alignment calibration algorithm but also underscores the system's capability to achieve precise multi-layer printing despite challenges posed by variations in jetting performance.

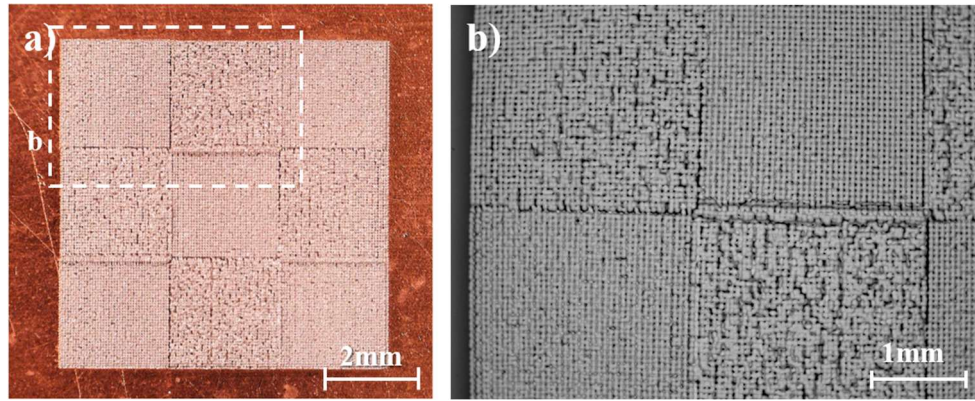


Figure 4.29 (a) Camera image of a 5-layer checkerboard pattern, made with both printheads using Sn (b) SEM image of the 5-layer checkerboard pattern

4.3 Summary of system development

This chapter outlined the development of the dual-head MetalJet system, with particular emphasis on the design and implementation of the control software and the validation of the system through initial experiments. As the first control system developed specifically for multi-material MMJ, it incorporates several features uniquely tailored to the process. The software design introduces a split user interface that separates certain functions to enhance system reliability, an efficient toolpath planning module that eliminates blank pixels, and a high-accuracy printhead alignment calibration algorithm adapted for MMJ. To further support multi-material printing, a “checkpoint + relative position” method was implemented for defining pattern locations, significantly reducing positioning errors during operation. After troubleshooting, the system was validated in initialise experiments, demonstrating successful jetting of Sn and Ag and achieving a printhead alignment accuracy within $7\mu\text{m}$. These results confirm both the reliability and precision of the MetalJet system and its effective customisation for multi-material applications. The successful initial experiments also mark the establishment of the world’s first multi-material MMJ system, providing a robust technical foundation for future research into process strategies and interfacial phenomena.

5 Development of printing strategies

This section demonstrates how tailored printing strategies in MMJ influence part density, surface roughness, and electrical conductivity. Based on these findings, a set of guidelines has been developed to assist in selecting appropriate strategies for specific objectives.

5.1 Optimal droplet spacing across strategies and substrate temperatures

Optimal droplet spacing (ds_{opt}) for each strategy at each substrate temperature was calibrated prior to printing. Taking the Normal strategy at $T_s = 150^\circ\text{C}$ as an example, the ds value was adjusted in $1\ \mu\text{m}$ increments to produce a series of samples for determining ds_{opt} . As shown in Figure 5.1 (a) and (d), when the ds was $5\ \mu\text{m}$ smaller than the optimal value, slight bulging of the surface was observed in the SEM image. With increasing ds , the surface roughness gradually decreased, reaching its lowest value at ds_{opt} , as illustrated in Figure 5.1 (b) and (e). However, when ds exceeded the optimal by $6\ \mu\text{m}$, surface roughness increased again and gaps appeared between droplets, as shown in Figure 5.1 (c) and (f).

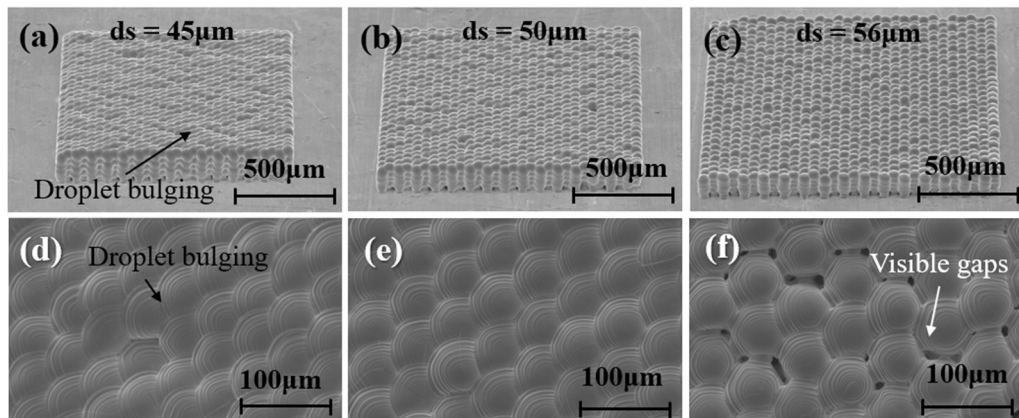


Figure 5.1 SEM image of Sn samples printed at squeezed, optimal and scattered droplet spacing on substrate temperature of 150°C

SEM images from the ds_{opt} calibration for other strategies and substrate temperatures are provided in Appendix Figure 6, Appendix Figure 7 and

Appendix Figure 8. In this study, the process window of ds is defined as the range between its upper and lower limits. The ds_{opt} together with their corresponding process windows are summarised in Figure 5.2. Normal, Staggering and Honeycomb all have $\pm 1\mu\text{m}$ tolerance at a $T_s = 150^\circ\text{C}$ and $1\mu\text{m}$ tolerance at $T_s = \pm 0.5\mu\text{m}$ tolerance at $T_s = 100^\circ\text{C}$. At a substrate temperature of 50°C , these three strategies showed no process window as printing failures were observed. The alternate strategy has $\pm 2\mu\text{m}$ process window in ds across all three substrate temperatures.

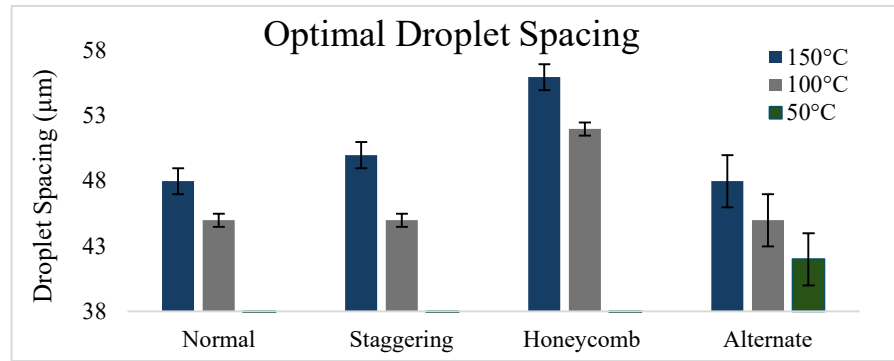


Figure 5.2 ds_{opt} value and its process window at substrate temperatures of 150°C , 100°C and 50°C

5.2 Surface texture and geometry features

The SEM pictures presented in Figure 5.3 to Figure 5.5 illustrate the 3D view and the top surface of samples fabricated by four different deposition strategies at a high (150°C), medium (100°C) and low (50°C) substrate temperature with ds_{opt} . Samples exhibited differences in thickness and length, which is due to the difference in applied ds . Samples produced using the Normal and Alternate strategies exhibited four flat side-surfaces, while those fabricated with the Staggering and Honeycomb strategies displayed two flat and two sawtooth-textured side-surfaces. At high and medium substrate temperatures, all four strategies created parts that retained the desired cubic shape, with dimensional deviation within $5\mu\text{m}$. The top surface of samples from all four strategies showed uniform droplet deposition, as shown in Figure 5.3 and Figure 5.4. As the substrate temperature decreased from 150°C to 100°C , no obvious changes in texture can be observed on the top surface, while on the side surface, the

boundaries of saw-teeth texture from Staggering and Honeycomb grew sharper. This was due to the reduced spreading of droplets at lower temperatures, as rapid cooling and solidification fixed the droplet contact line in place, resulting in sharper sawtooth features.

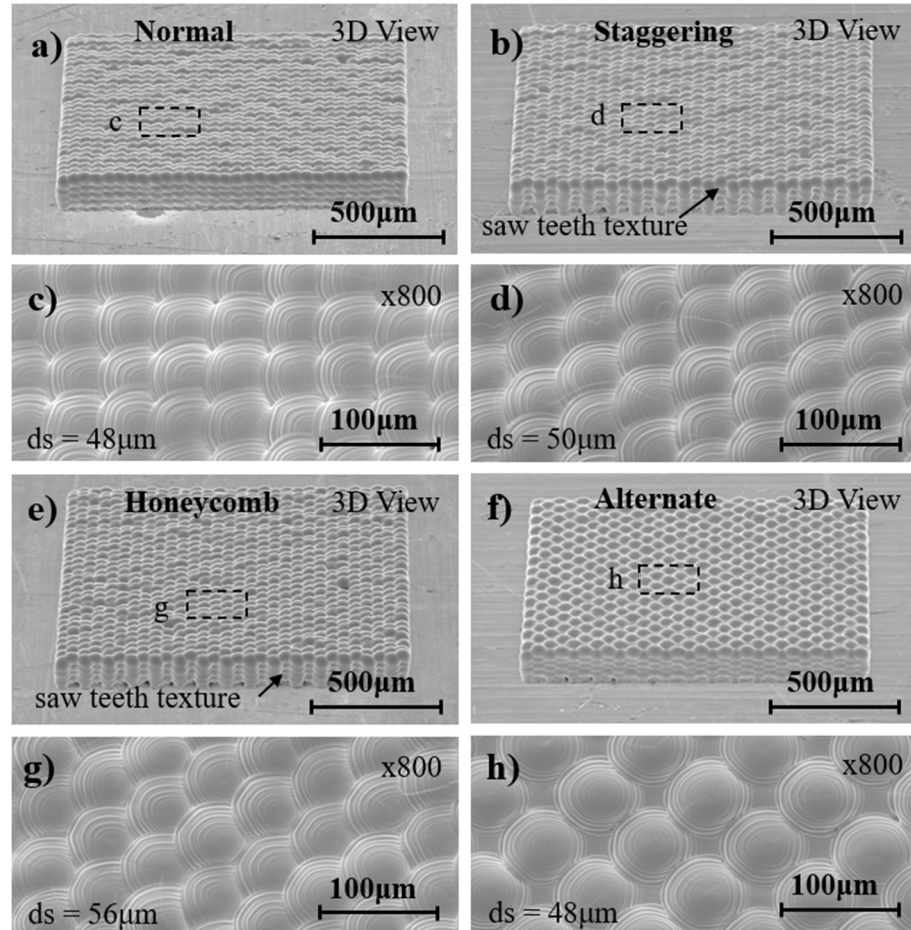


Figure 5.3 SEM images of 3D views and surface texture of samples printed with Normal, Staggering, Honeycomb and Alternate strategy at $T_s = 150^\circ\text{C}$

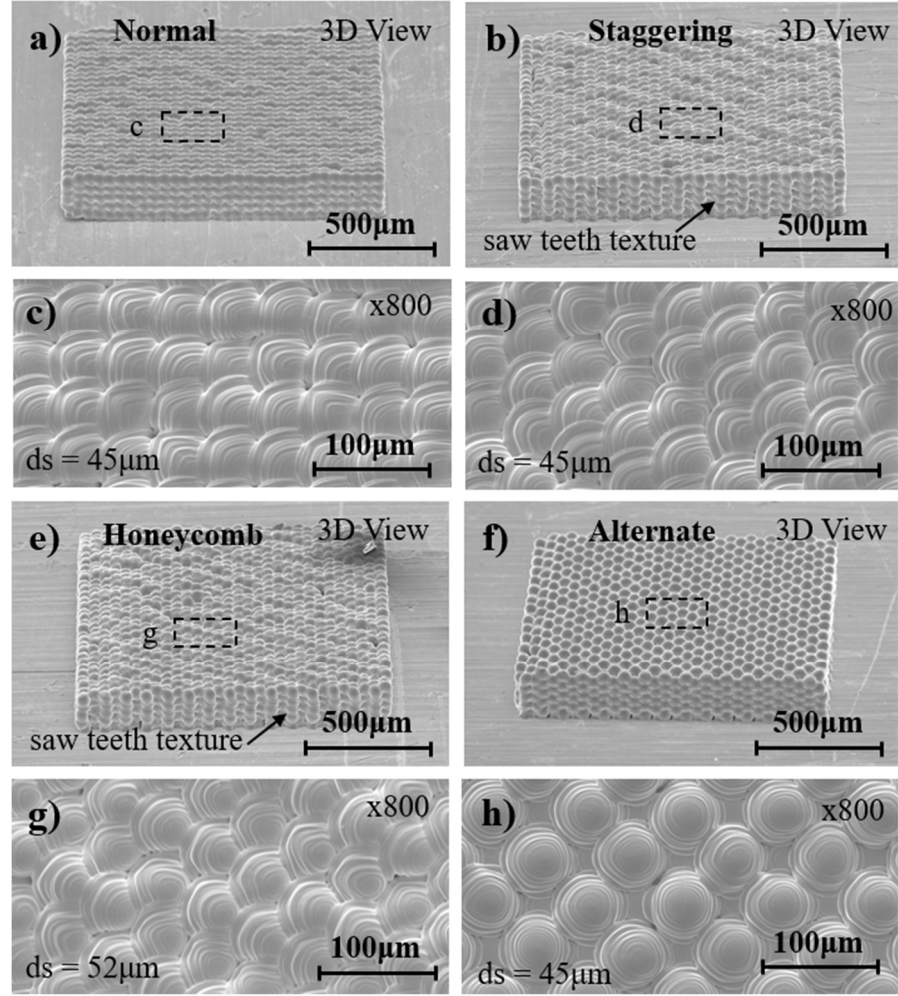


Figure 5.4 SEM images of 3D views and surface texture of samples printed with Normal, Staggering, Honeycomb and Alternate strategy at $T_s = 100^\circ\text{C}$

When the substrate temperature further decreased to 50°C , noticeable pores appeared between the droplets on the top surface of samples printed with the Normal and Staggering strategies, as shown in Figure 5.5. The Staggering strategy exhibited an irregular texture on the surface. In this strategy, the space required for a droplet to spread along the printing direction (Y) is smaller than in the across-trace direction (X), as shown in Figure 3.14. At low substrate temperatures, the droplet solidification time is reduced, limiting droplet spreading. As a result, the liquid droplets could not fill the gaps between traces in the Staggering strategy, causing an irregular morphology of the top surface. In the Normal strategy, insufficient droplet spreading leaves pores between the droplets. Attempts to reduce the ds to compensate for these gaps will lead to droplets “stair up” along the trace direction.

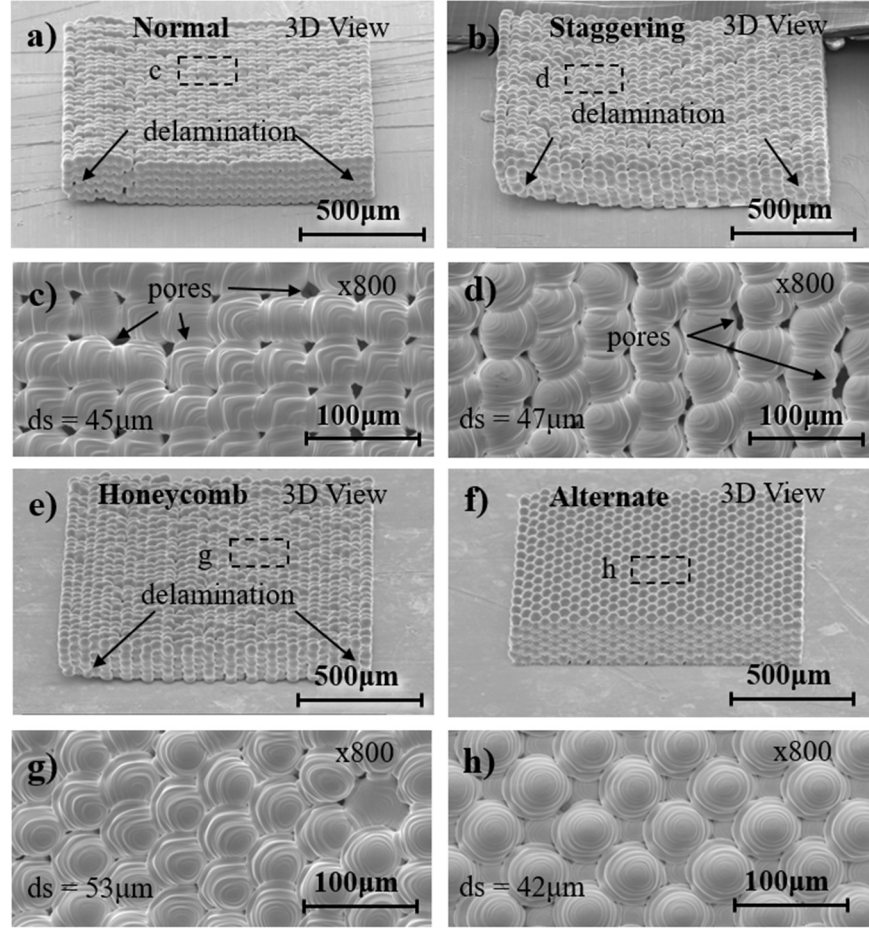


Figure 5.5 SEM images of 3D views and surface texture of samples printed with Normal, Staggering, Honeycomb and Alternate strategy at $T_s = 50^\circ\text{C}$

In addition to the appearance of surface pores, delamination from the substrate was observed in all strategies at low substrate temperatures, except for the Alternate strategy. Samples printed by the Normal and Honeycomb strategy (Figure 5.5 (a) and (e)) experienced delamination, primarily at the corners. The Staggering strategy (Figure 5.5 (b)) also caused delamination at the corners, with a noticeable warping of the printed parts. This delamination can be attributed to a combination of reduced droplet-substrate bonding [46] and residual stress accumulation [162]. Due to the absence of simulation tools, this section will provide a quantitative analysis of residual stress accumulation during the deposition process for different printing strategies. Firstly, the droplet-substrate bonding weakens at low substrate temperatures [46], creating the necessary conditions for delamination to occur. In the Normal, Staggering, and Honeycomb strategies, samples are constructed incrementally, layer by

layer, trace by trace. Consequently, during cooling, the deposited material contracts along the horizontal direction. However, this contraction is restricted by the substrate or the previously deposited layers, resulting in tensile residual stress in the horizontal plane. This stress is particularly pronounced at the edges, where the constraint is weaker. As a result, delamination in these three strategies typically initiates at the four corners of the sample. This heat accumulation and dissipation are in line with previous computational studies[113], [119]. In contrast, the Alternate strategy uses a checkerboard deposition pattern, where a liquid droplet contacts both the substrate and four neighbouring solidified droplets that are evenly distributed around it, which significantly alters the heat transfer pathways of the droplets. This uniform distribution of neighbouring droplets allows heat to dissipate in multiple directions, mitigating thermal gradients in any single direction and reducing the accumulation of localised thermal stress.

5.3 Inner voids distribution of samples from 4 strategies

Voids distribution at various strategies

To assess the distribution of internal voids for each printing strategy, CT imaging was conducted on samples printed at a substrate temperature of 150°C. This substrate temperature was chosen because it allows better droplet spreading, thus minimising the impact of droplet spreading and highlighting the effect of packing strategy on void formation. Figure 5.6 (a) to (d) displays the 3D renderings of solid bodies for samples fabricated using four different deposition strategies. The corresponding internal voids are presented in 3D volume renderings in Figure 5.6 (e) to (h). Although voids or pores cannot be observed from the top surfaces of all the samples, the extracted 3D renderings clearly reveal internal voids within all four samples. The volume of the inner voids was estimated by counting void voxels. Among these strategies, the Normal strategy exhibited the most widely distributed internal voids and the largest total pore volume at 3068 μm^3 . In comparison, the Staggering, Honeycomb, and Alternate strategies showed significantly lower pore volumes, measured at 351 μm^3 , 464 μm^3 , and 686 μm^3 , respectively.

To better illustrate the void distribution in these samples, X-Y sectional tomography views are shown in Figure 5.6 (i) to (j). These sections, located 145 μm and 152 μm above the substrate, correspond to the middle of the fourth and fifth layers, as indicated by the arrows in Figure 5.6 (a) to (d). In the samples printed with the Normal strategy, voids are consistently distributed across layers (Figure 5.6 (i)). To investigate the formation of these periodically distributed voids, a magnified image of the pore within the circle in Figure 5.6 (i) was captured, as shown in Figure 5.6 (m). This region was selected near the boundary, since the contour of the boundary helps identify droplet positions. It can be observed that the voids in the Normal strategy form in the central region of the spatially simple cubic packing of eight adjacent droplets. The pore formation mechanism in the Normal strategy is as follows: during the printing of a single trace, subsequent droplets are deposited next to already solidified droplets, causing minimal re-melting at the interface [113], [120]. This results in a side profile with protrusions and concavities (contours M1 and M2 in Figure 5.6 (m)) instead of a smooth, straight line. When the adjacent trace is deposited, a droplet (M4 in Figure 5.6 (m)) contacts neighbouring droplets within the same trace (M3) and the previous trace (M2). Solidification begins at the contact points, as indicated by the arrows. However, the corner formed by droplets M1, M2, and M3 cannot be filled before M4 solidifies, leading to the formation of a pore. Since heat dissipation primarily occurs through the substrate (or the previous layer), these voids consistently form at the interfaces between adjacent layers.

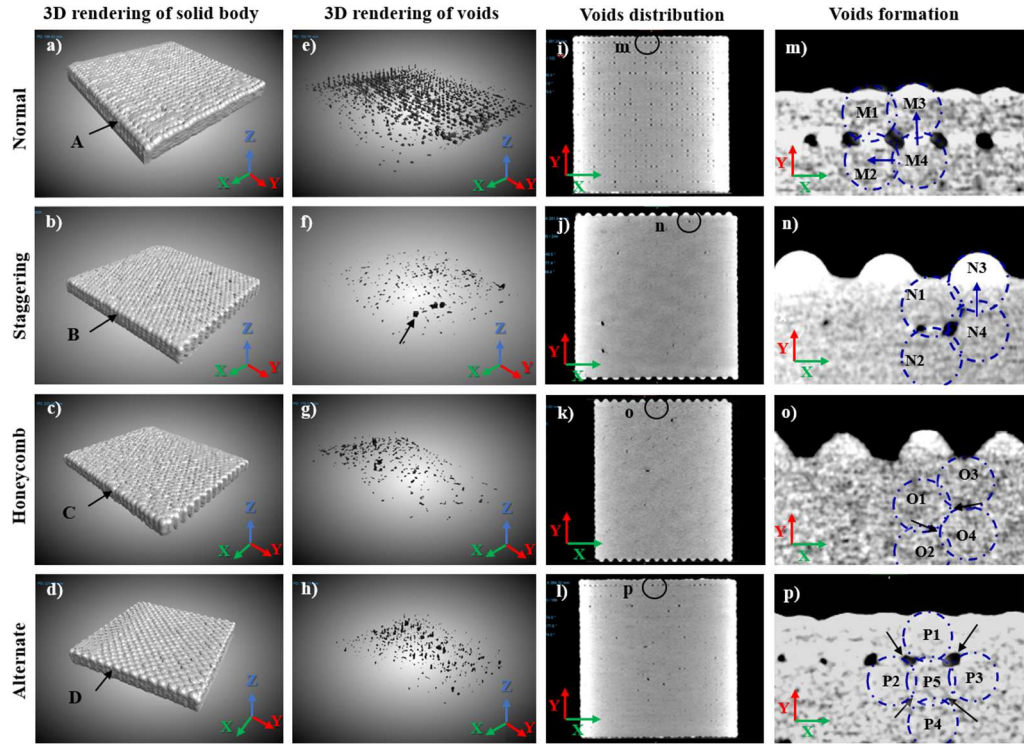


Figure 5.6 Samples from four strategies at 150°C substrate temperature (a)-(d) 3D volume rendering of the samples, (e)-(h) 3D volume rendering of voids, (i)-(l) X-Y cross-sectional image between layer 4 and layer 5 (m)-(p) X-Y cross-sectional image demonstrating Normal, Staggering, Honeycomb and Alternate pore formation

The distribution of voids in the Staggering, Honeycomb and Alternate samples is sparser and more irregular compared to the Normal strategy, with most voids being smaller in size (Figure 5.6(j)-(l)). Some larger voids, indicated by the arrows in Figure 5.6 (f), likely result from irregular conditions during droplet deposition, such as variations in droplet size. In the Staggering strategy, as shown in, as shown in Figure 5.6 (n), the region formed by droplets N1, N2, and N3 is an obtuse angle, which is less influenced by surface tension, making it easier for the liquid metal to fill compared to the near-right-angle region seen in the Normal strategy. The Honeycomb strategy, with its inherent close-packing arrangement that theoretically reaches 90.7% filling rate, ensures efficient pore elimination. As shown in Figure 5.6 (o), the solidifying droplet (O4) only needs to fill the two corners indicated by the black arrows to eliminate internal voids. The Alternate strategy introduces more flexibility in droplet deposition within the same layer, particularly in the across-layer (Z) direction. Figure 5.6 (p)

presents a cross-sectional view in the XY plane for this strategy. The previously deposited droplets (P1, P2, P3 and P4) formed a “pinning” to hold the solidifying droplet (P5). Solidification begins from the contact points between droplet P5 and droplets P1–P4, as well as the substrate or the underlying droplet. This situation makes it difficult for droplet P5 to spread into the corner formed by the solidified droplets, potentially leading to pore formation at the locations indicated by the black arrows in Figure 5.6 (p). However, no periodic pore formation was observed under high substrate temperatures.

Voids distribution at various substrate temperatures (T_s)

To examine the effect of substrate temperature on inner porosity, samples printed using the Alternate strategy at 150°C, 100°C, and 50°C were analysed from CT datasets. The Alternate strategy was chosen because it is the only one that avoids residual stress at low substrate temperatures. Figure 5.7 (a) to (c) display the 3D renderings of the solid structures, and Figure 5.7 (d) to (f) show the reconstructed 3D models of the extracted voids. As the substrate temperature decreased, both the volume and distribution of cavities increased. At substrate temperatures of 100°C and 150°C, inner voids were distributed irregularly, whereas at 50°C, the inner cavities between droplets became periodically distributed. To ensure consistency across different strategies, all samples were taken from the X–Y cross-section at the interface between the fourth and fifth layers, although sampling at other layers would not affect the results. The cross sections of these samples are provided in Figure 5.7 (g) to (i), highlighting the locations where inner voids formed. Although the pore formation mechanism remains consistent in the Alternate strategy, its generation becomes consistent at the bottom of each deposited droplet at low substrate temperatures. The recurring presence of these cavities suggests that the corners, as shown in Figure 4 (i), are difficult to fill due to limited droplet spreading at low temperatures. This challenge also arises from the reduced solidification time at lower substrate temperatures, which prevents the liquid droplet from spreading sufficiently to fill these corners before solidifying. The density of these three samples is measured as $99.11 \pm 0.05\%$ for $T_s = 150^\circ\text{C}$, $99.02 \pm 0.05\%$ for $T_s = 100^\circ\text{C}$ and $98.13 \pm 0.05\%$ for 50°C, which correlates with the observed inner pore formation.

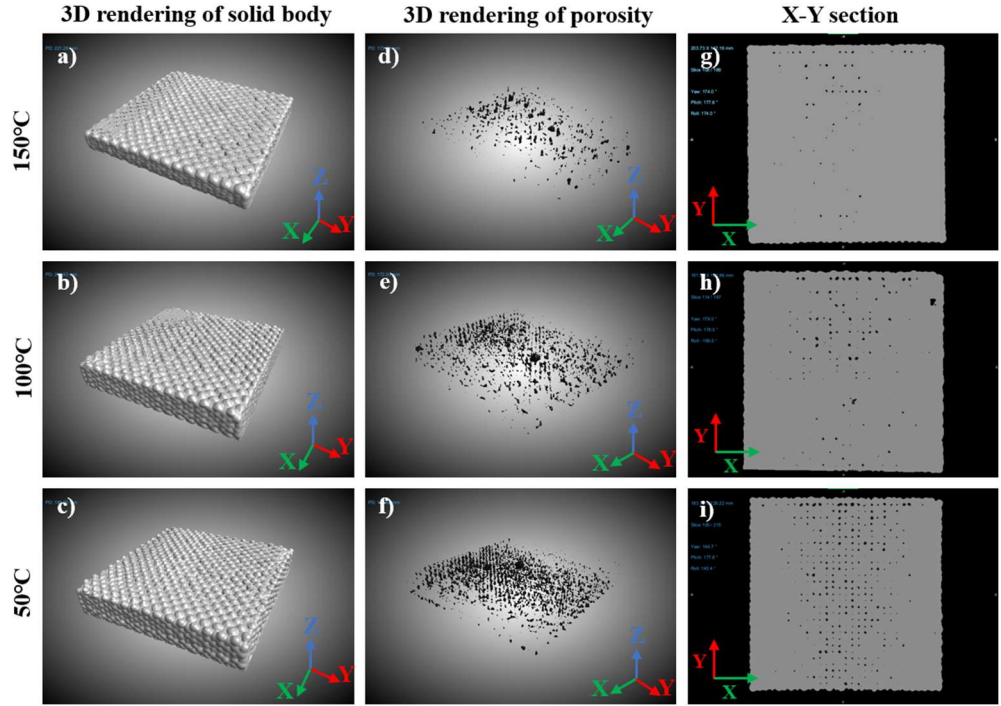


Figure 5.7 CT scan result of the Alternate strategy from 50°C to 150°C substrate temperature. (a)-(c) 3D volume renderings of the samples (d)-(f) 3D volume rendering of voids (g)-(i) virtual X-Y cross-sectional image between the third and the fourth layers

5.4 Surface roughness of samples printed at $T_s = 150^\circ\text{C}$

Surface data for samples produced using the four strategies at high substrate temperatures were attained from reconstructed 3D models obtained through CT image segmentation. The reconstructed surfaces of Normal, Staggering, Honeycomb, and Alternate are presented in Figure 5.8 (a-d). To highlight surface features, such as cavities, the surfaces were inverted so that peaks in the images now represent actual cavities. These reconstructed surfaces reveal peaks and valleys corresponding to the depressions and protrusions on the actual sample surface.

The Normal and Alternate strategy sample surfaces show larger peak-valley distances (R_z), which are $9.13\mu\text{m}$ and $6.97\mu\text{m}$, respectively. However, the peak-valley distribution on the Alternate surface is less dense compared to the Normal strategy. To provide a more representative measure of surface quality, R_a was used instead of R_z , as R_z is highly sensitive to extreme values and only reflects

the maximum peak-to-valley distance rather than the overall distribution density. Ra values of these surfaces are calculated, as displayed in Figure 5.8 (e). The Staggering strategy results in the lowest average Ra value of $4.41\mu\text{m}$, followed by the Honeycomb at $4.93\mu\text{m}$ and the Alternate at $5.50\mu\text{m}$. Although the Normal strategy exhibits the highest Ra value of $5.79\mu\text{m}$, its maximum and minimum Ra values are comparable to those of the Alternate strategy.

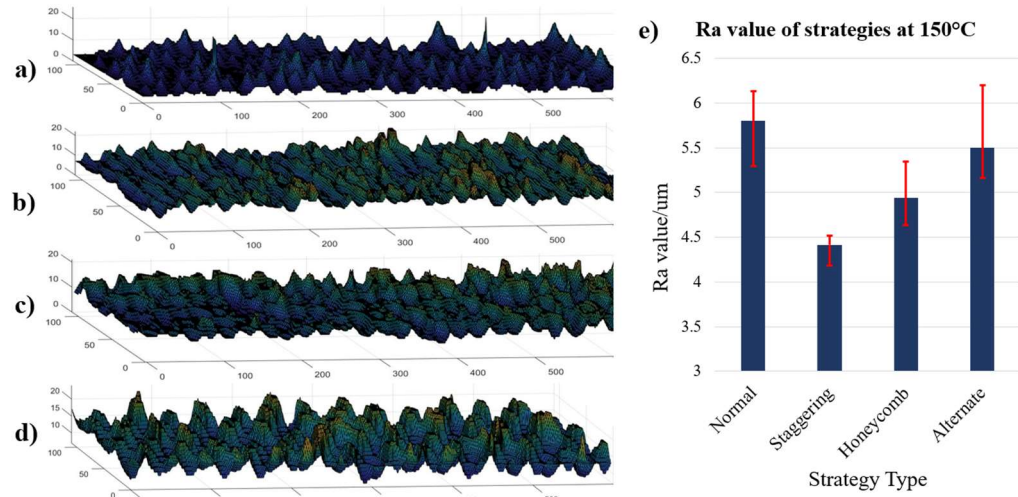


Figure 5.8 (a) – (d) Reconstructed upside-down surfaces from samples of Normal, Staggering, Honeycomb and Alternate strategy. (e) Ra value of the corresponding strategies at $T_s = 150^\circ\text{C}$

Surface roughness is influenced by the droplet spreading behaviour in each strategy. In the Normal strategy, the liquid droplet may have difficulty filling the corners or sharp edges of already solidified droplets during spreading, resulting in lower places or valleys on the surface. The staggered arrangement in the Staggering and Honeycomb strategies allows better filling of recessed regions, reducing unfilled corners and lowering surface roughness. In the Alternate strategy, the surface roughness is primarily caused by its checkerboard deposition pattern. The droplets from the second round of deposition are supported by the four neighbouring droplets from the first round, forming surface protrusions. These protrusions follow a checkerboard distribution across layers, which explains why the peaks and valleys on the Alternate surface are less densely packed compared to those of the Normal strategy.

5.5 Electrical conductivity and density

Electrical conductivity is an important parameter for 3D-printed samples intended for electronic applications. Figure 5.9 illustrates the electrical conductivity of long-bar samples produced using the four deposition strategies at a substrate temperature of 150°C. The electrical conductivity of the Normal printing strategy samples is measured as $7.97 \times 10^6/\Omega\text{m}$, which is significantly lower than the electrical conductivity values of samples produced using the other three methods. Samples from the Staggering, Honeycomb and Alternate strategies exhibit electrical conductivity values of $8.95 \times 10^6/\Omega\text{m}$, $9.00 \times 10^6/\Omega\text{m}$ and $8.96 \times 10^6/\Omega\text{m}$, which have less than 2% gap to the conductivity of bulk Sn ($9.17 \times 10^6/\Omega\text{m}$).

The grey histogram in Figure 5.9 presents the measured density values for samples printed using the four strategies at high substrate temperature. The Normal strategy results in the lowest density, which is $98.01 \pm 0.05\%$. The Staggering and Honeycomb strategies achieve near-complete densification, which are $99.67 \pm 0.05\%$ and $99.73 \pm 0.05\%$, respectively. The Alternate strategy also achieves high density, measured at $99.11 \pm 0.05\%$, though it remains slightly lower than the Staggering and Honeycomb strategies.

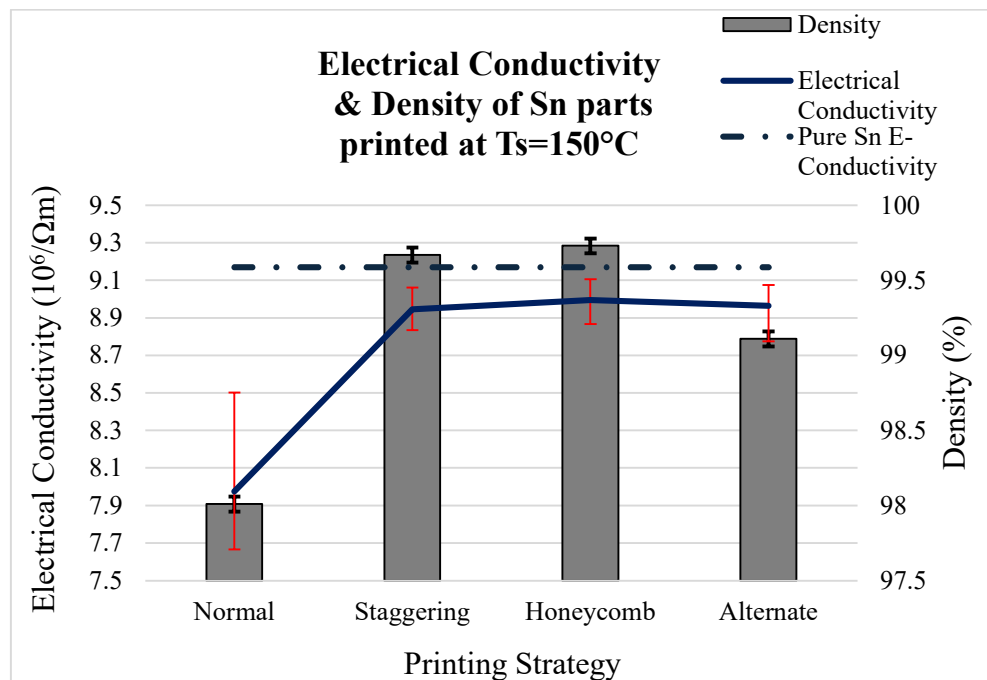


Figure 5.9 Resistivity measurement for four different strategies at Ts = 150°C

A strong correlation is observed between a sample's density and its electrical conductivity. As density increases, electrical conductivity improves. This relationship arises because voids act as non-conductive regions, forcing electrons to bypass them during conduction. This increases the current's path length and overall resistance. Furthermore, reducing porosity increases the metallic cross-sectional area actively involved in conduction, thereby providing wider pathways for electron flow. This minimises localised resistive losses during the conduction, leading to enhanced electrical performance.

5.6 Summary of printing strategy development

The printing strategy section introduces novel printing strategies applicable to most droplet-based AM methods, offering an alternative approach to reduce internal voids without solely relying on process parameter adjustments. Four different printing strategies were employed to print the samples at three distinct substrate temperatures. To evaluate the samples printed by these strategies, the geometry integrity and surface texture of the samples are first characterised, followed by observation of the inner voids distribution using CT. Furthermore, the surface roughness and electrical conductivity of the samples were measured. All Staggering, Honeycomb and Alternate strategies achieved densities above 99% and electrical conductivities exceeding 97% of the bulk material. Among them, the Staggering strategy yielded the lowest Ra value of 4.41 μm , followed by Honeycomb, Alternate, and Normal. Notably, the Alternate strategy was the only one capable of mitigating residual stress effects at $T_s = 50^\circ\text{C}$.

Each strategy has its own strengths, and the choice in practice should be guided by the requirements of the specific application. For instance, when density alone is the main concern, Staggering, Honeycomb, and Alternate strategies are all suitable. However, the Alternate strategy doubles the printing time, and Honeycomb relies on a specialised slicer for hexagonal pixels, making Staggering the most practical option. In electronics applications, where both density and surface finish are critical, the strategy must be chosen based on sidewall requirements: Alternate is preferable when smooth sidewalls are

essential, while Staggering remains suitable when the sawtooth side profile is acceptable. Overall, this study provides the first systematic evaluation of printing strategies in MMJ. By establishing the strengths and limitations of each strategy, it equips users with a clear framework to select the most suitable approach for different applications, thereby broadening the applicability of MMJ in both structural and functional components.

6 Sn-In Multi-material study

This chapter presents the results of the multi-material investigation. The work focuses on understanding the formation of interfaces between dissimilar materials, optimising parameters for multi-material printing, and demonstrating representative sample fabrication.

6.1 Interface study of dissimilar materials

A fundamental step towards enabling multi-material MMJ is to elucidate how interfaces between dissimilar metals are formed. In this study, the nozzle temperatures were maintained at 650 °C for Sn and 630 °C for In, with T_s set to 80 °C. The ejected droplet radius is measured at 25 ± 0.5 μm for Sn and $30\pm0.5\mu\text{m}$ for In from the strobic camera. The investigation characterised the microstructure and elemental distribution across the Sn–In interface and provided insights into its underlying formation mechanisms.

6.1.1 Dissimilar droplets deposited with contact

The SEM image of a printhead alignment sample is demonstrated in Figure 6.1 (a), where each of the 36 indium droplets was perfectly aligned with its corresponding tin counterpart, verifying the effectiveness of the alignment calibration. A closer examination provided in Figure 6.1 (b) shows the 3D view of a single In droplet on a Sn droplet structure, from which a base at the bottom and a dome on the top can be seen.

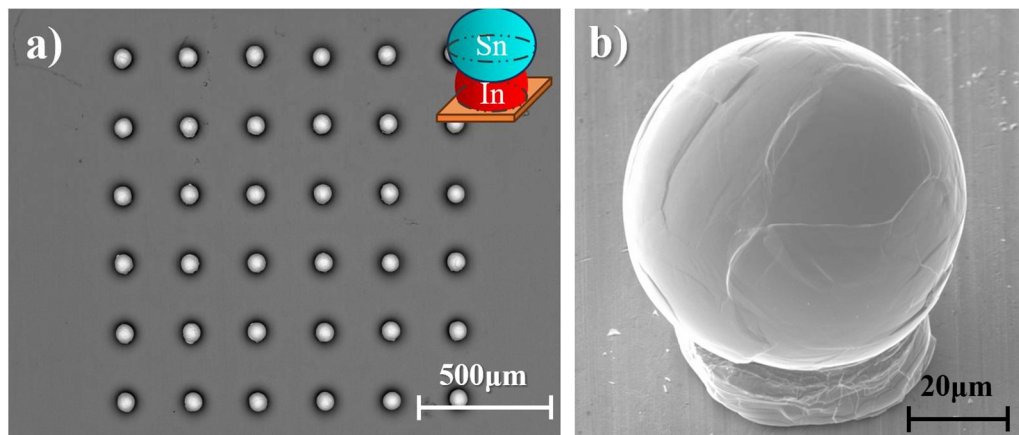


Figure 6.1 SEM images of Indium droplet(s): (a) The printed In, (b) 3D view (at 60° angle) of one of the droplet-on-droplet samples.

Figure 6.2 (a) and (d) showcase SEM images of “In-first-Sn-second” samples and “Sn-first-In-second” samples printed in arrays on an 80°C Cu substrate. The droplet-by-droplet sample is fabricated using a spacing of 40 μm (with 15 μm overlap applied in printing settings). In the detailed analysis of droplet-by-droplet deposition, SEM images and EDX mappings have provided insightful views into the arrangement and interaction between Sn and In droplets. The corresponding EDX mappings presented in Figure 6.2 (b) and (e) illustrate the top view of these configurations, with Sn highlighted in blue and In in red.

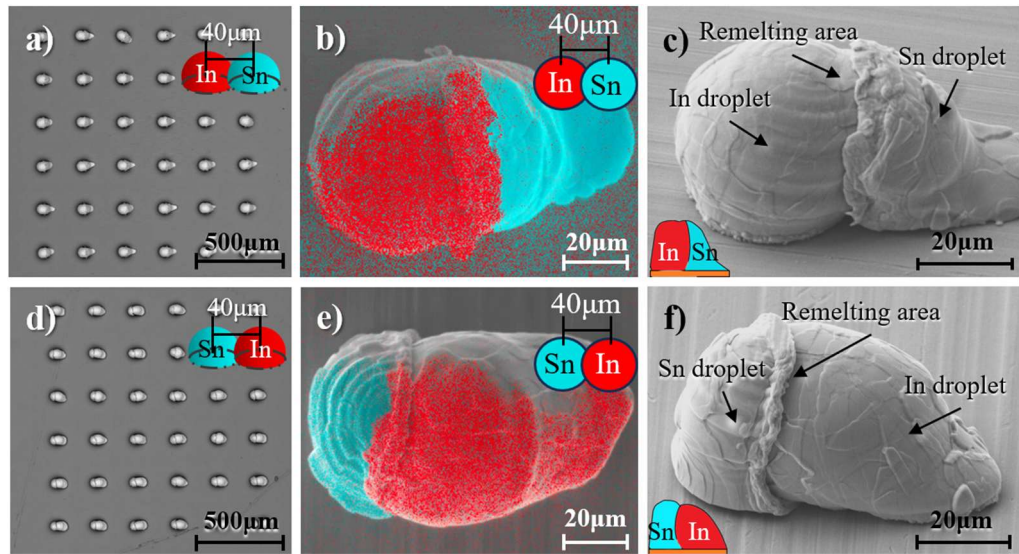


Figure 6.2 (a) SEM image of “In-first-Sn-second” array (b) SEM image of “Sn-first-In-second” array (c-d) EDX mapping of the top view of one of the In-first-Sn-second and Sn-first-In-second samples (e-f) SEM image of the 3D views of In-first-Sn-second and Sn-first-In-second samples.

SEM images in Figure 6.2 (c) and (f) provide a 3D perspective of both configurations. Each sequence captures the phenomenon where the droplet deposited subsequently appears to collapse or be drawn into the previously deposited droplet. This observation indicates a significant displacement of the later-deposited droplet towards the earlier-deposited dissimilar droplet. This displacement was not considered to be caused by the error in alignment, as this has already been ensured by the previous alignment verification step. At the juncture where the two droplets meet, the later deposited In droplet exhibits elongation towards the Sn side, while the Sn droplet consistently shows a rim

formation at the contact point. This interaction suggests a dynamic remelting process might have occurred at the interface of the two different materials, where the heat from the latter droplet may partially remelt the interface of the first, facilitating a strong metallurgical bond. The presence of a rim formation and elongation of the droplet near the indium side further highlights the complexity of thermal and material dynamics in multi-material MetalJet printing. To fully understand these interactions and the subsequent effects on material integrity and joint quality, further cross-sectional analysis is necessary.

6.1.2 Microstructure and element distribution at cross sections

To delve deeper into the interfacial interactions occurring during multi-material deposition, cross-sections of structures where In droplets are deposited next to Sn droplets and vice versa were meticulously analysed. SEM images presented in Figure 6.3 (a) and (b) highlight the cross-sections, and the disappearance of the boundary of original droplets reveals visible signs of remelting, which implies that alloying took place as the adjacent droplets made contact. This is further indicated by the presence of a segregation line, suggesting a mixing of the metals at the interface.

EDX mapping, shown in Figure 6.3 (c) and (d), and the subsequent quantitative element distribution plots in Figure 6.3 (e) to (h), delineate the specific elemental concentrations along the dashed lines from the previous figures. These analyses reveal robust metallurgical bonding at the interface with no discernible pores or cracks. Both Sn and In demonstrate an even distribution within the In-rich regions, though a concentration gradient is apparent in the Sn-rich areas. The elemental analysis along the four dashed lines indicates that the In-rich regions in both configurations consist of approximately 59% In and 41% Sn. This composition aligns closely with the dashed line in the Sn-In phase diagram depicted in Figure 6.4 (a) [163] corresponding to near-saturation levels [164] of Sn in In at the eutectic temperature of 120°C. At room temperature, this composition is supposed to be the $\beta+\gamma$ phase, whose microstructure was illustrated in Figure 6.4 (b). However, due to the overlapping characteristic X-ray emission lines of Sn and In, EDX struggles to distinctly quantify small amounts of indium even under high electron beam energies [165]. In particular,

the $L\alpha$ emission line of Sn lies at approximately 3.44 keV, while that of In is at 3.28 keV. The proximity of 0.16 keV of these peaks leads to significant spectral overlap, making it difficult to reliably separate the contributions of the two elements in mixed regions. This limitation hampers the precise determination of Sn and In distribution within the In-rich phase. This is why the In-rich phase showed a uniform colour region, no matter how fine the focus of the EDX is adjusted. In this way, X-ray Photoelectron Spectroscopy (XPS) should be considered for future characterisation. To be noticed, a gradient in composition can be found between the Sn-rich phase and In-rich phase, where Sn composition changes from 41% to 71% and 72% to 41% for each printing sequence. The element concentration is not 100% because the length of the FIB milling cross-section is shorter than the length of the diffusion area. The presence of a smooth gradient rather than a sharp interface indicates that interdiffusion occurred between these two phases.

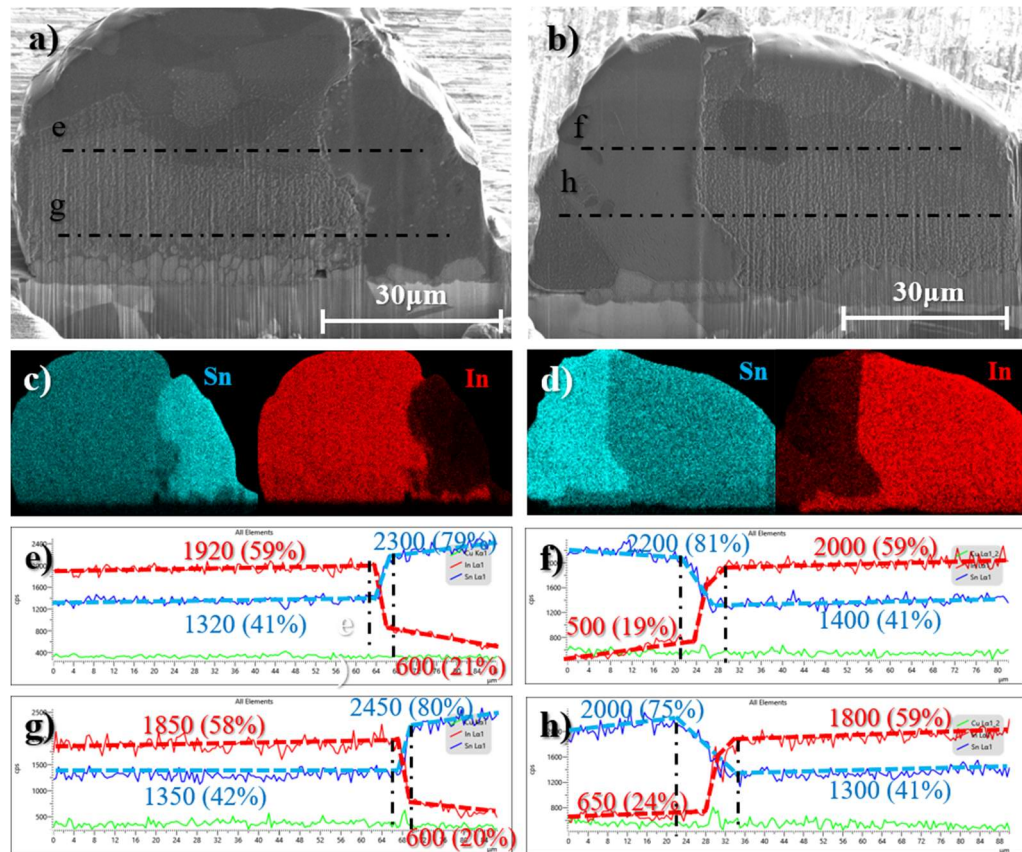


Figure 6.3 (a)-(b) SEM image of sections of In-first-Sn-second and Sn-first-In-second samples (c)-(d) EDX mapping showing Sn and In element distribution (e)-(h) Element concentration of Sn and In at dashed line e, f, g and h.

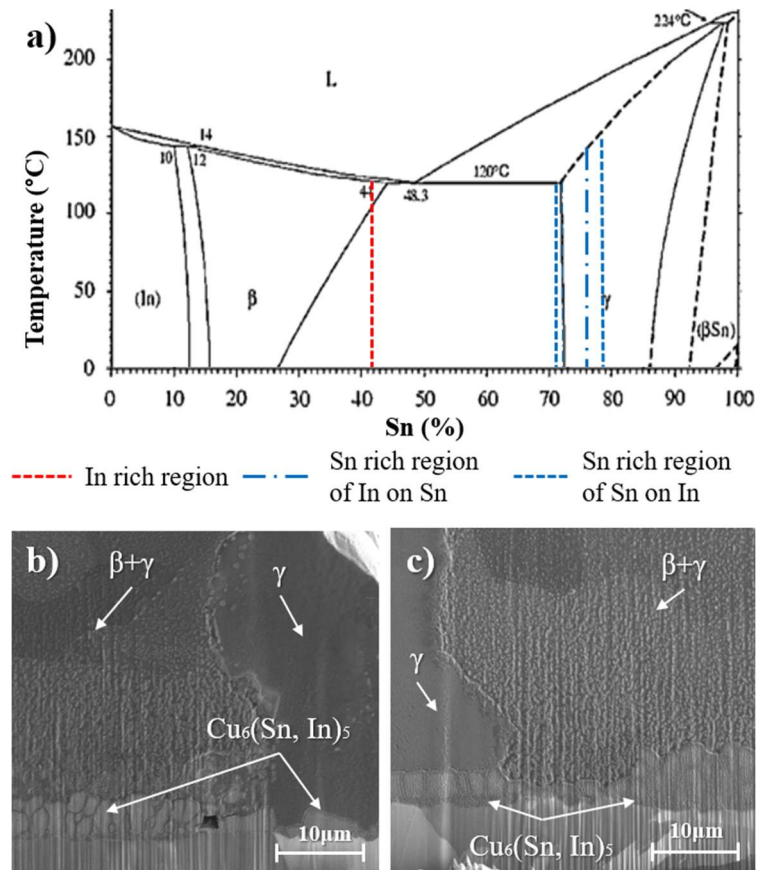


Figure 6.4 (a) Sn-In phase diagram, adapted from [166] (b)-(c) microstructure at interface

The Sn-rich regions from the In-first-Sn-second configuration exhibited a composition of 29% In and 71% Sn, whereas the Sn-first-In-second structure revealed a slightly different composition of 24% In and 76% Sn. These compositions belong to the γ phase on the Sn-In phase diagram, as delineated by the blue dashed line in Figure 6.4 (a). At room temperature, it is anticipated that the Sn-rich phase in both structures predominantly consists of a γ phase, depicted in Figure 6.4 (b). The similar elemental concentrations near saturation in both the Sn-rich and In-rich sides suggest a broad fusion zone, potentially as extensive as the droplets themselves, which is wider than 90 μm. This uniformity in concentration underscores a substantial interdiffusion between the droplets, indicative of robust metallurgical bonding irrespective of the deposition sequence.

Further to the basic alloy phases, IMCs of a scallop-structure were also identified near the substrate, as evidenced in Figure 6.4 (b) and (c). These IMCs,

irrespective of their placement under the indium-rich or tin-rich phases, maintain a compositional ratio of approximately Sn42%In58%, which closely approaches the saturated concentration Sn48%In52% [166]. Observations from Figure 6.3 (c) and (d) indicate that the IMCs located under the tin-rich phase tend to possess a higher indium content than the tin-rich phase itself. This phenomenon could be attributed to the growth dynamics of IMCs: in the ternary alloy solder interactions of Sn, In, and copper (Cu), copper typically reacts with Sn in the liquid alloy first, forming a hexagonal lattice of η Cu₆Sn₅ [165], [167], [168] which can be described as: $6\text{Cu} + 5\text{Sn} \rightarrow \text{Cu}_6\text{Sn}_5$. Subsequently, indium atoms replace the positions of tin atoms within this IMC lattice through atomic substitution [167], resulting in the formation of Cu₆(Sn, In)₅. The In segregation in IMCs likely relates to the differing maximum solubility of indium within these phases, though further data are required to substantiate this hypothesis comprehensively.

6.1.3 Interface formation mechanism

The characterisation results have facilitated the development of a simplified model that decreases the deposition dynamics when a Sn droplet is printed adjacent to an In droplet, and vice versa. This model, depicted in Figure 6.5 (a) to (c), can be divided into three stages: Remelting on contact, alloy solidification and phase segregation.

In the first stage, the second droplet is deposited and contacts the first droplet and substrate. Based on previous studies, the contact temperatures are estimated to be 630°C for Sn and 585°C for In [45], [46], leading to the partial remelting of the first, as shown in Figure 6.5 (a).

In the second stage, during the interface temperature declines from these initial contact temperatures to the eutectic temperature of 120°C, an expansion of the liquid phase towards the solid phase is observed. Besides the direct re-melting during heat transfer, this expansion is also attributed to the concentration at the solid interface reaching the composition of 52%Sn / 48%In, referring to the phenomenon observed in Sn-In joint fabrication [169]. The interdiffusion continues until the concentration distribution attains saturation. At the interface,

the products of the eutectic reaction [170], the In-rich phase saturated are $\beta+\gamma$ phase (48%Sn / 52%In) and γ phase (73%Sn / 27%In).

During the second stage, as the volume of the liquid metals increases, those two bulks of liquid metals tend to decrease their surface tension by merging into a larger droplet. This causes the phenomenon that the second deposited droplet merges into the previously solidified droplet. Wetting plays an important role during the process, as the liquid-substrate surface tension acts as a stopping force to this coalescence. This indicates that the better the substrate-droplet wetting, the less likely the droplet merge occurs.

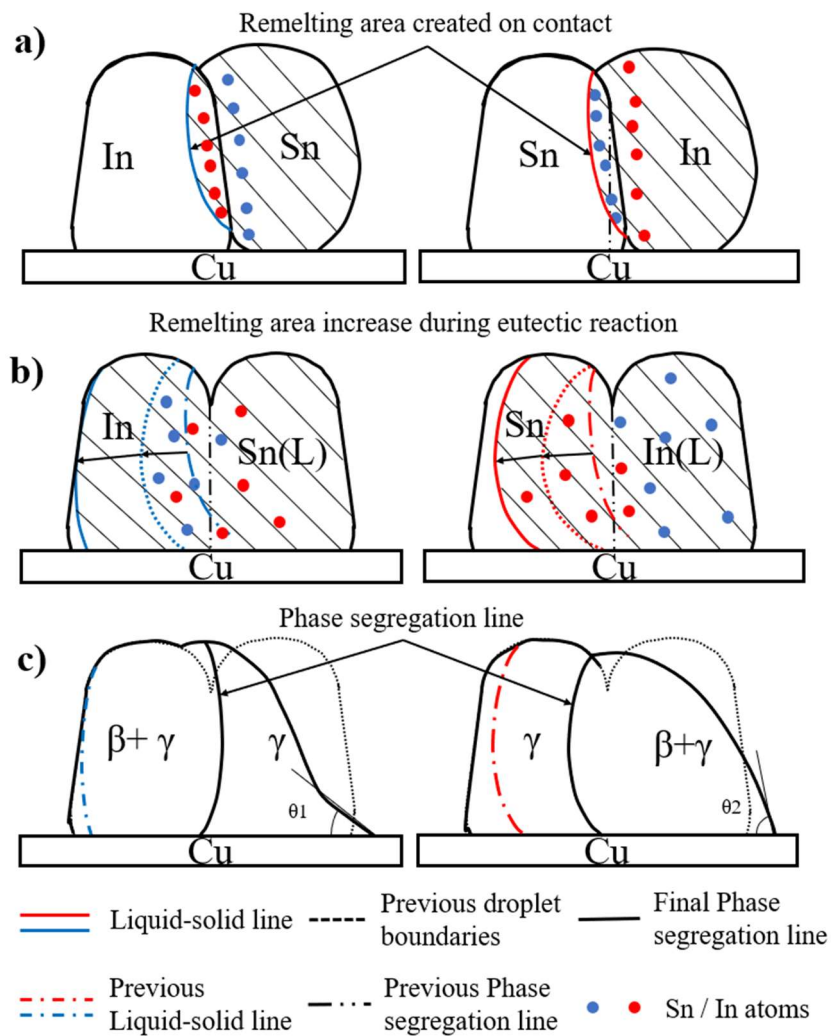


Figure 6.5 (a)-(c) Diagram of In-first-Sn-second and Sn-first-In-second model
(d) Diffusion rate difference of Sn and In from 20°C to 600°C

The last stage is the phase segregation during solidification, following the decrease in interface temperature below 120°C. The diffusion rate of Sn within the Sn-In alloy system is significantly higher than that of In, as depicted in Figure 6.6, influencing the phase segregation line to finally sit towards the Sn-rich side. As the temperature continues to drop from 120°C to room temperature, the Sn-rich phase crystallises into a γ phase, whereas the In-rich region turns into a $\beta+\gamma$ phase. The phase segregation line position at the solidified droplet is influenced by the difference in diffusion rate.

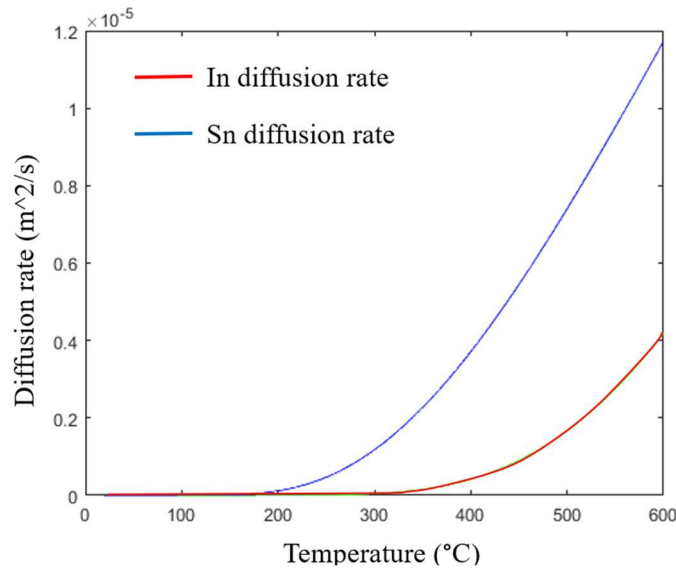


Figure 6.6 Diagram showing the diffusion rate difference of Sn and In from 20°C to 600°C

An intriguing observation in the multi-material MetalJet printing process is that, irrespective of the sequence of deposition, the droplet deposited subsequently is invariably drawn towards the earlier deposited droplet, resulting in their coalescence. This phenomenon is a combination effect of remelting, wetting and diffusion. Figure 6.7 (a) and (b) illustrate the contours of the In-first-Sn-second and Sn-first-In-second samples, respectively, where an evident gap marked by a line shadow forms due to this coalescence effect. Actual printings confirmed this kind of expectation. Figure 6.7 (c) shows a part printed by Sn and In on a Cu substrate, where Sn is deposited first and then In. As pointed out by the arrows, the In droplets coalesced towards the solidified Sn droplets' side, leading to the formation of a gap in the In region.

The gap resulting from the droplet coalescence in the Sn-first-In-second sequence appears smaller compared to that in the In-first-Sn-second configuration. This difference could stem from the varying amounts of remelted liquid generated in each sequence. Given that tin (Sn) and indium (In) have similar densities and heat capacities, the variation in the volume of remelted liquid is attributed to their different melting points, 231.9°C for Sn and 156.6°C for In. Consequently, the In-first-Sn-second sequence tends to produce a greater quantity of liquid metal upon remelting and cause a more serious coalescence than the Sn-first-In-second sequence.

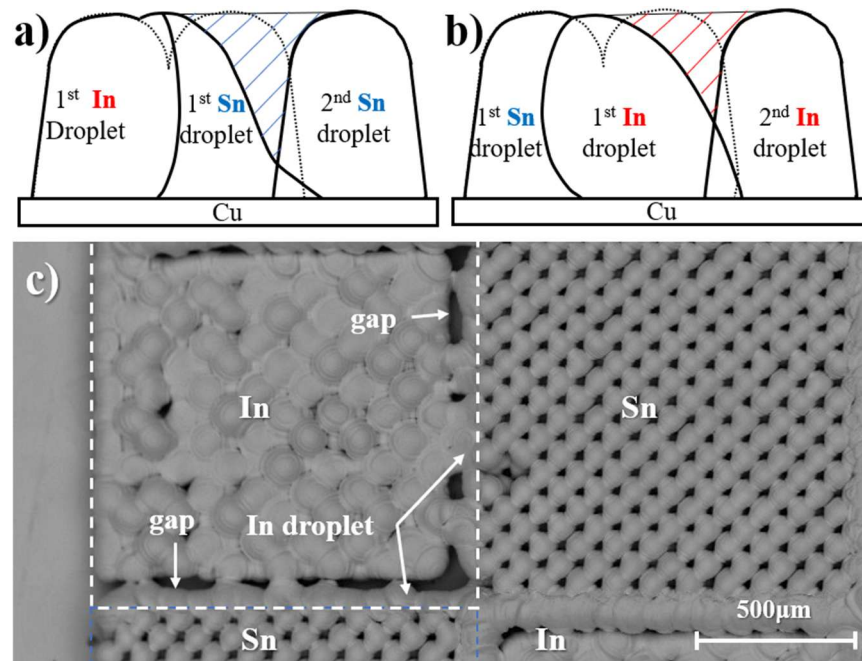


Figure 6.7 Diagram of the gap formation caused by droplet displacement (a) 2nd Sn droplet deposit aside In-first-Sn-second sequence structure (b) 2nd In droplet deposit aside Sn-first-In-second structure (c) SEM images of defects caused by droplet coalescence at Sn-In joint

The following sub-sections address the mitigation of droplet coalescence through two approaches: optimising process parameters, specifically substrate temperature, deposition ratio, and deposition sequence, and implementing tailored printing strategies for multi-material fabrication.

6.2 Process parameters and printing strategy study

Based on the understanding of single material printing, the role of substrate temperature in multi-material MMJ printing appears to be pivotal, particularly because it significantly impacts the solidification dynamics, affecting both the inter-diffusion duration and the solidification morphology of dissimilar metals

6.2.1 Effect of substrate temperature

Figure 6.8 (a) to (c) displays the appearance of Sn droplets, originally positioned $40\mu\text{m}$ from the centroid of In droplets at substrate temperatures of 100°C , 80°C , and 60°C , respectively. At all examined temperatures, the Sn droplets exhibit a distinct tail-shape structure that leans towards the In droplet, suggesting a directional solidification influenced by the proximity of the different metals. This orientation results in a physical gap in the printed structure where another droplet deposited adjacent to the tail-shaped structure might not seamlessly coalesce. As the substrate temperature decreases, the remelted area between the droplets, which is typically devoid of ripples, becomes narrower, pointing to a reduction in solidification time.

Figure 6.8 (d) to (f) shows the morphology of In droplets deposited $40\mu\text{m}$ away from Sn droplets at the same range of substrate temperatures. From these images, no significant changes in the top view of the Sn-first-In-second samples are noted as the substrate temperature is decreased. However, the top view cannot represent the story of the whole interface, thus cross-sectional study is needed to better evaluate the effect of T_s .

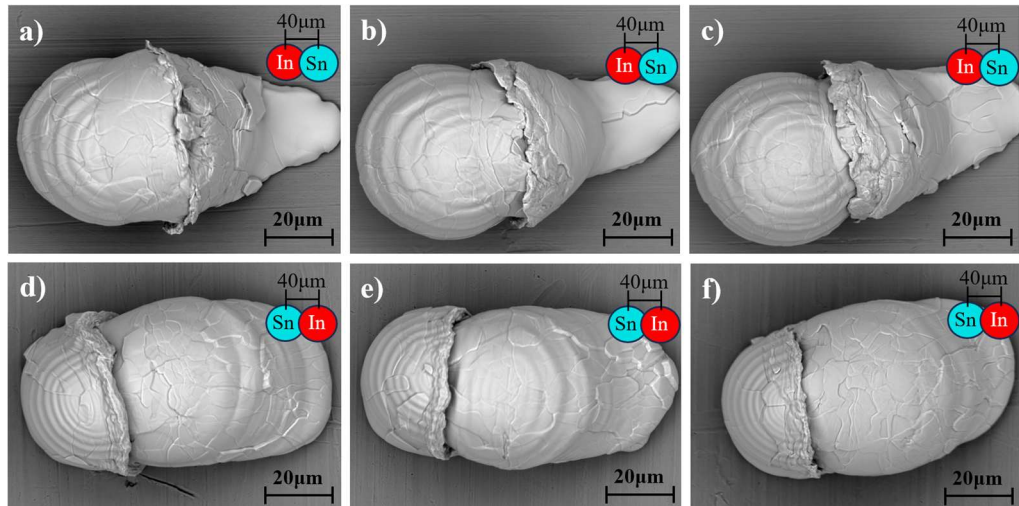


Figure 6.8 (a)-(c) In-first-Sn-second samples at substrate temperature of 100°C, 80°C and 60°C. (d)-(f) Sn-first-In-second samples at substrate temperature of 100°C, 80°C and 60°C

For the samples of In-first-Sn-second, Figure 6.9 (a), (c) and (e) display SEM images of cross-sections from samples printed at substrate temperatures of 100°C, 80°C, and 60°C. These images reveal no apparent cracks or gaps along the phase segregation line, indicating stable interfaces across varying temperatures. In the In-rich regions of these samples, the elemental composition consistently showed approximately 41% Sn and 59% In across all temperatures, aligning with the composition of β phase and the $\beta+\gamma$ phase at room temperature in the phase diagram, as evidenced in the ion beam images. Conversely, in the Sn-rich regions, a concentration gradient is evident; at positions close to the phase segregation line (points A1, C1, and E1), the concentration for all samples was around 71% Sn and 28% In. This uniformity across samples suggests that both Sn-rich and In-rich phases reached saturation during alloying, indicative of robust metallurgical bonding. Towards the outer edges of the Sn-rich regions (points A2, C2, E2), the In concentration decreased from 20% to 12%, as outlined in Table 6.1. This shift suggests a predominance of the γ phase, with a reduction in In concentration likely due to shorter alloying times at lower substrate temperatures. Interestingly, a small pore was observed at the base of the In-rich region in samples at 100°C and 60°C. The formation of this pore did not correlate directly with changes in substrate temperature, likely due to the solidification angle of the In droplet being greater than 90 degrees, preventing the subsequently deposited Sn droplet from completely filling the gap created by the preceding droplet and the substrate.

Table 6.1. In the concentration ratio in the Sn-rich region at the marked point

	Sn-rich region of In-first-Sn-second samples		Sn-rich region of Sn-first-In-second samples	
	Left end	Right end	Left end	Right end
100°C	A1 29±0.5%	A2 20%±0.5	G1 18±0.5%	G2 28±0.5%
80°C	C1 29±0.5%	C2 17±0.5%	I1 12±0.5%	I2 28±0.5%
60°C	E1 28±0.5%	E2 12±0.5%	K1 7±0.5%	K2 28±0.5%

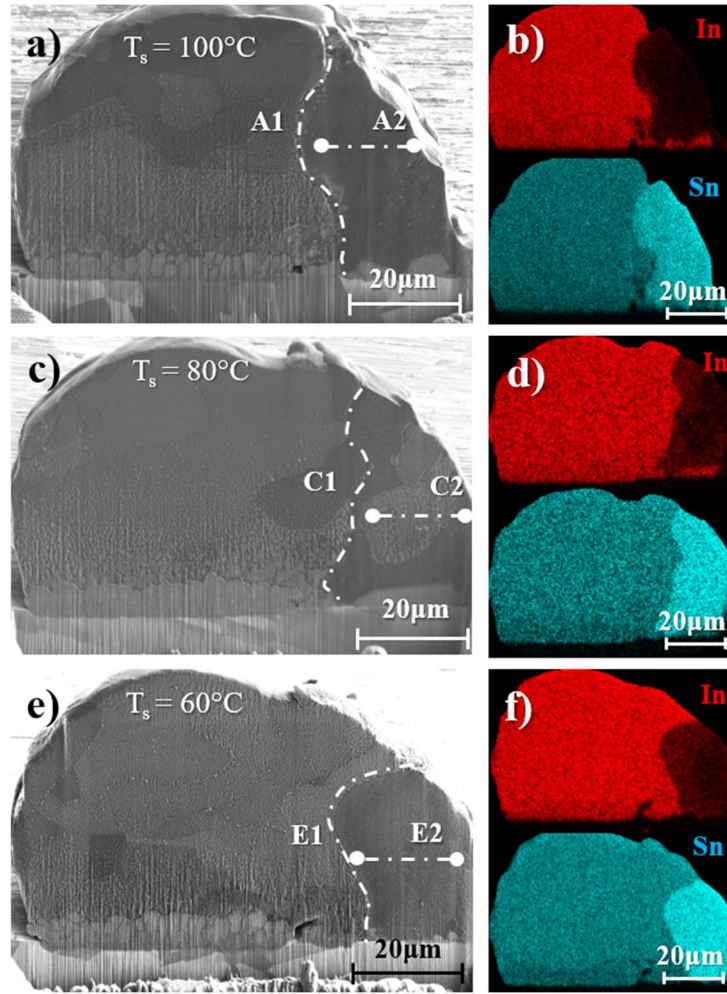


Figure 6.9 (a) (c) (e) SEM image of the cross section of In-first-Sn-second samples at substrate temperatures of 100°C, 80°C and 60°C separately. (b) (d) (f) EDX Mapping of Sn and In element distribution at the cross section of In-first-Sn-second samples at T_s of 100°C, 80°C and 60°C

For I Sn-first-In-second samples, Figure 6.10 (a) (c) and (e) showcase the Sn and In distribution for each substrate temperature, with corresponding EDX maps in Figure 6.10 (b), (d) and (f) show the EDX maps at sections. Similar to the In-first-Sn-second results, the In-rich regions consistently demonstrated a homogenous mixture close to 41% Sn and 59% In. At the phase segregation line (A4, C4, E4), the In concentration remained around 28%, suggesting strong metallurgical bonding. As substrate temperature decreased, the concentration of Sn in the In-rich phase diminished (A3, C3, E3) from 18% to 7%, reflecting a

shift in the phase structure from predominantly γ phase at higher temperatures to a transition phase from γ to β -Sn at lower T_s , as depicted in the phase diagrams.

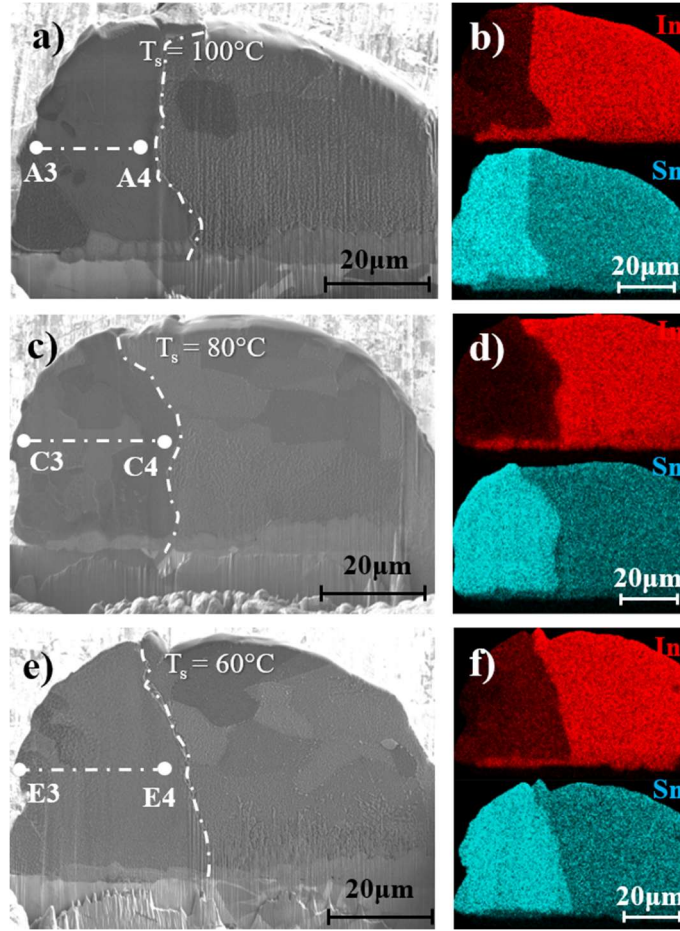


Figure 6.10 (a) (c) (e) SEM image of the cross section of Sn-first-In-second samples at substrate temperatures of 100°C, 80°C and 60°C separately. (b) (d) (f) EDX Mapping of Sn and In element distribution at the cross section of Sn-first-In-second samples at T_s of 100°C, 80°C and 60°C

It was noted that lower substrate temperatures (60°C) led to reduced diffusion between the materials, mitigating but not eliminating droplet merging issues. The sequence of deposition had a pronounced effect on this merging; the Sn-first-In-second sequence exhibited significantly less droplet merging than the In-first-Sn-second sequence. Consequently, when aiming for optimal interface quality between Sn and In, a substrate temperature of 60°C and an Sn-first-In-second deposition sequence is recommended. This approach ensures stronger interfacial bonding and better control over material behaviour during the printing process.

6.2.2 Effect of deposition ratio

Another strategy to mitigate droplet coalescence is to deposit a droplet between two already solidified droplets. In this method, the solidified droplets on either side are expected to pull the newly deposited droplet outward during solidification, thereby reducing the likelihood of gap formation. SEM images provided in Figure 6.11 (a) and (b) illustrate the morphological outcomes when a Sn droplet is deposited between two In droplets, and conversely, an indium droplet is placed between two tin droplets, at a substrate temperature of 60°C. These configurations are henceforth referred to as Sn-between-In and In-between-Sn, respectively.

From the top view of the Sn-between-In sample in Figure 6.11 (a), it is noticeable that the two adjacent In droplets have undergone partial remelting. This indicates a significant interaction between the Sn droplet and the In droplets, likely facilitated by the thermal conditions and proximity of the droplets, which promote remelting. Conversely, the In-between-Sn sample shows that the previously deposited Sn droplets have partially melted and merged with the centrally deposited In droplet. Despite the slight asymmetry in the structure, the central droplet in either strategy is evenly influenced by the Sn droplets on either side, showing no signs of displacement error, unlike the samples from the In-first-Sn-second and Sn-first-In-second configurations.

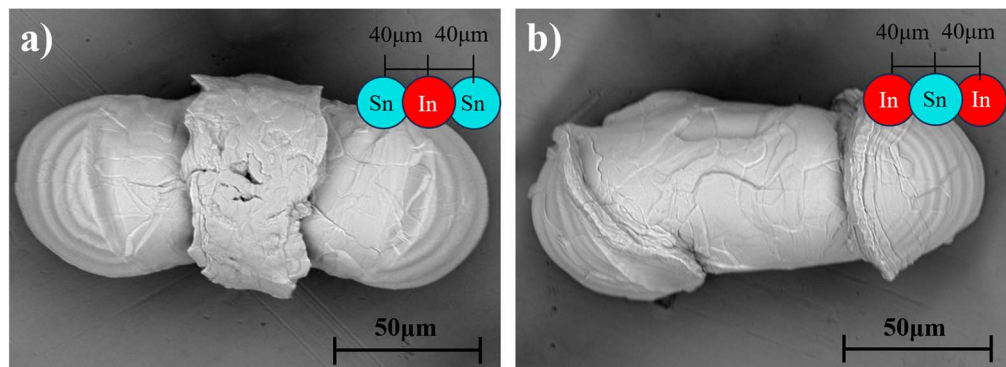


Figure 6.11 (a) In droplet deposit between two Sn droplets at substrate temperature of 60°C (b) Sn droplet deposit between two In droplets at substrate temperature of 60°C

To further analyse the bonding dynamics between dissimilar metal droplets, EDX mapping and FIB-SEM techniques were employed on the cross sections

of the samples. Figure 6.12 (a) and (e) present the ion beam images showing half of the vertical cross-sections for the Sn-between-In and In-between-Sn samples, respectively. These images reveal that the boundaries of previously deposited droplets have fully melted together, with no discernible gaps or voids at the interface, indicating effective metallurgical bonding. Figure 6.12 (b) and (f) detail the distribution of Sn and In elements within these structures. Subsequent Figure 6.12 (c) to (d) and (g) to (h) display the element concentrations along designated dashed lines within the cross-sections, providing a detailed view of the elemental distribution across the interfaces.

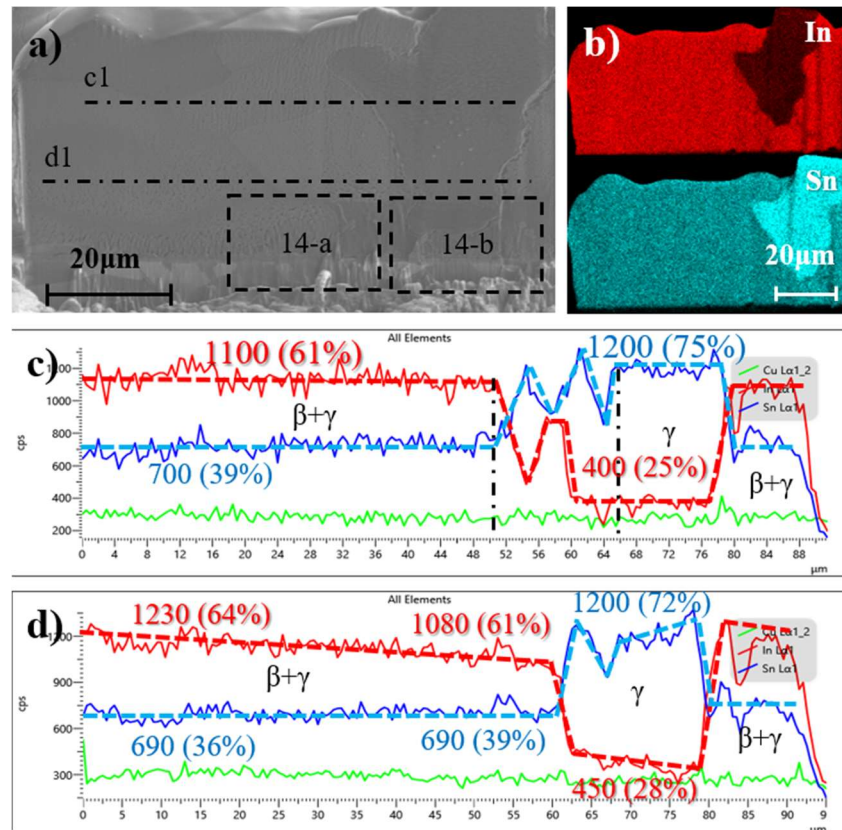


Figure 6.12 (a) SEM image of "1 In between 2 Sn" at substrate temperature of 60°C (b) Sn-In element distribution at cross section of "1 In between 2 Sn" (c)-(d) Line scan of Sn-In element distribution at dash line c1 and d1

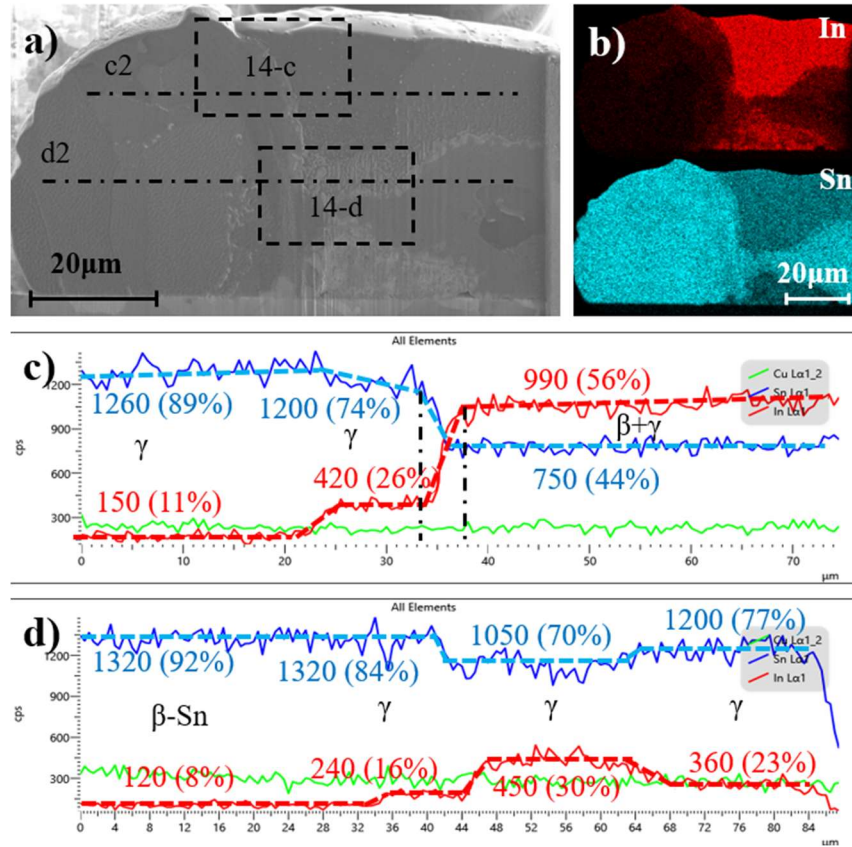


Figure 6.13 (e) SEM image of “1 Sn between 2 In” at substrate temperature of 60°C (b) Sn-In element distribution at cross section of “1 In between 2 Sn” (c)-(d) Line scan of Sn-In element distribution at dash line c2 and d2

In the Sn-between-In sample, the Sn-rich region appears significantly smaller than the In-rich region in the cross-sectional EDX images, consistent with the higher diffusion rate of Sn into liquid In compared to In into liquid Sn, as discussed in the previous section 6.1.3. For instance, along the dashed line c1 in Figure 6.12 (a), the In-rich region maintains a steady concentration of 61% In and 39% Sn, showing no gradient. Conversely, a slight gradient is observed in the In-rich region along dash line d, where In concentration slightly decreases from 64% to 61% and Sn concentration increases from 36% to 39% from left to right, indicating full diffusion of Sn into the In-rich phase before solidification. The composition analysis of these regions suggests a $\beta+\gamma$ phase in the In-rich areas and a uniform γ phase in the Sn-rich areas, as located in dashed rectangle 14-a and 14-b in Figure 6.12 (a) and the microstructures are demonstrated in Figure 6.14 (a) and Figure 6.14 (b), respectively. The In-rich regions are

connected at the bottom of the section through a corridor composed of $\beta+\gamma$ phases, shown in Figure 6.14 (b).

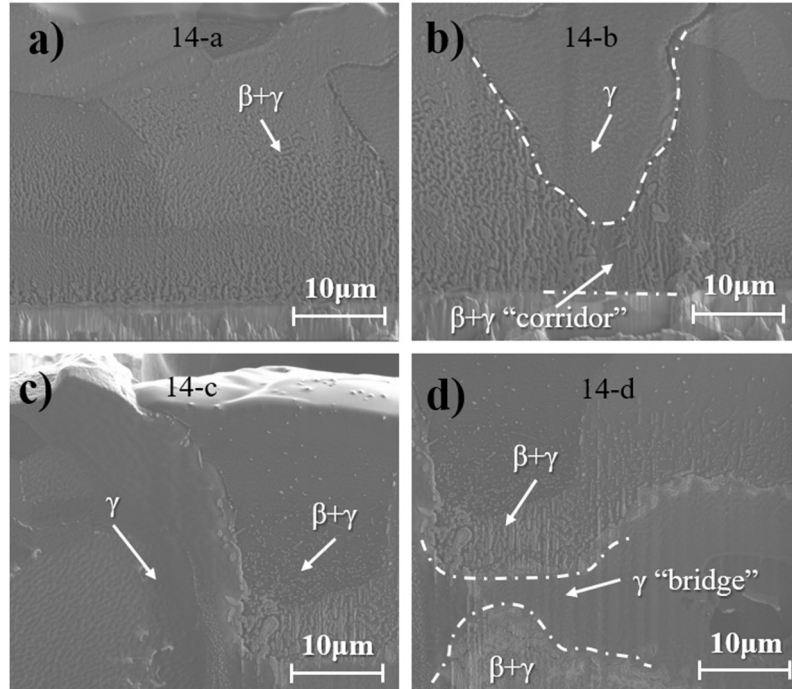


Figure 6.14 SEM image showing the microstructure in the dashed rectangle in 14-a, 14-b in Figure 6.12 (a) and 14-c, 14-d in Figure 6.13 (a)

For the In-between-Sn sample, as depicted in dashed rectangle 14-d in Figure 6.13(a), a Sn-rich "bridge" connecting the two Sn-rich regions across an In-rich region is observed, indicating dynamic interactions during solidification. The Sn concentration transitions from a β Sn phase (92% Sn, 8% In) at the left end to a γ phase (70% Sn, 30% In) across the bridge, as shown in Figure 6.13 (c) and (d). This bridge's composition aligns with the γ phase in the phase diagram, while the In-rich regions exhibit a $\beta+\gamma$ phase, detailed in Figure 6.14 (c).

This complex formation of the "corridor" and "bridge" suggests that remelting and re-solidification play significant roles in defining the microstructural characteristics of these multi-material interfaces. In the Sn-between-In configuration, the corridor forms at the substrate level because the remelted In from both sides fills the gap before the Sn droplets can spread to that position. In contrast, in the In-between-Sn setup, liquid In reaches the substrate first, followed by the remelted Sn from both sides, forming a bridge during their diffusion in the liquid phase.

6.2.3 Printing strategy for multi-material printing

From section 6.1.3, it has been verified that a gap will be formed at an Sn-In joint due to droplet coalescence. It has been verified that this kind of coalescence can only be reduced but not eliminated by decreasing substrate temperature or adjusting deposition sequence. A straightforward solution can be carried out that compensates for the gap by adding an overlap at the joint. In this way, two strategies are developed.

In the first strategy, as shown in Figure 6.15 (a), the borders of the patterns were expanded using a slicing tool, which includes adjustments in both the ds and input bitmap. This strategy is named “Slicing strategy” according to its approach. A checkerboard pattern with extra 20-30 μm overlap compensation at the interface joint is displayed in Figure 6.15 (b). However, the SEM image shown in Figure 6.15 (c) revealed that though some joints were successfully compensated, the others (pointed by arrows) bumped up and formed an “edge”. This is because the actual overlap exceeded the optimal value of 5-10 μm . This strategy faces the difficulty brought by the “slicing error” mentioned in section 4.1.4, Figure 4.11. When this slicing error adds to the 2-5 μm deposition error (which is at an acceptable value), the overall error will easily exceed 10 μm , causing too much or too little overlap to the actual printed part.

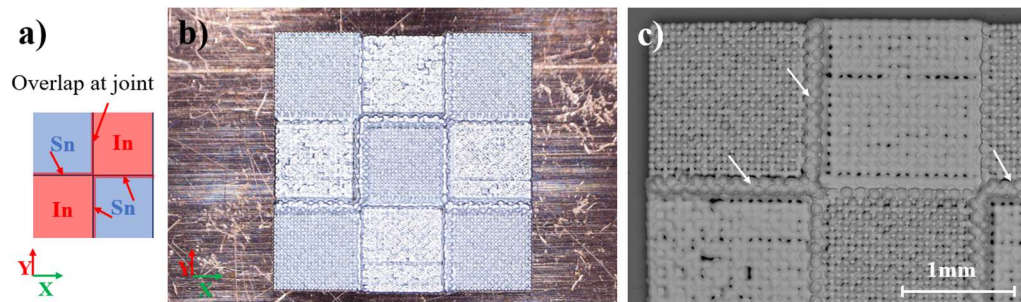


Figure 6.15 (a) Diagram of multi-material strategy 1: increase overlap at joint
(b) Camera image of checkerboard pattern printed on Cu substrate by strategy 1
(c) SEM images showing the edges formed by overlapping

The second strategy compensates the gap via printing with printing using a squeezed ds at 70% value of ds_{opt} using the Alternate strategy, as shown in Figure 6.15 (d). As mentioned in section 5, the Alternate strategy shows a wide

process window of ds , allowing droplets to be accumulated at small droplet spacing. This kind of squeezing ds allows the droplets at the joint to automatically compensate for the gap by themselves. In this way, this strategy is named by “Squeezed-Alternate” strategy. 1-layer and 3-layer patterns were demonstrated in Figure 6.15 (e). From the SEM images of the surface texture of the 1-layer part, the whole surface shows no gaps or edges, indicating that it is a successful way of depositing multi-materials in MMJ.

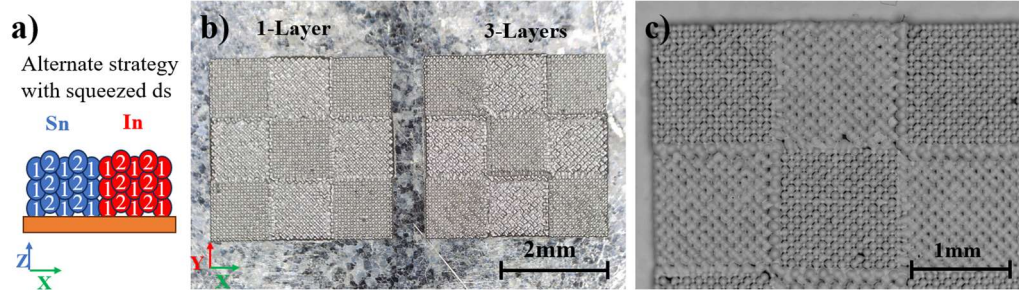


Figure 6.16 (a) Diagram of multi-material strategy 2: Alternate printing strategy with squeezed ds applied (b) Camera image of 1-layer and 3-layer checkerboard pattern (c) Surface texture of 1-layer checkerboard pattern fabricated by strategy 2

6.3 Multi-material printing demonstration

An interdigitated structure is printed with Sn and In on a Cu substrate to demonstrate the system’s ability to print multi-material parts. In this design, Sn and In regions were intentionally kept separate to prevent coalescence between the two materials. The structure, illustrated in Figure 6.17 (a) and (b), was generated from a 185×185 -pixel bitmap and constructed over 60 layers. Each finger measured three pixels in width, with a three-pixel gap between adjacent fingers. The optimised ds were determined to be $52 \mu\text{m}$ for In and $48 \mu\text{m}$ for Sn. However, to ensure better alignment during multi-material printing, a uniform droplet spacing was adopted. The value selected was $48 \mu\text{m}$, corresponding to Sn’s optimal spacing, since In droplets exhibit a longer solidification time and a wider acceptable range for ds . Based on this spacing, the intended gap width was approximately $144 \mu\text{m}$.

The final printed structure measured $7.4 \text{ mm} \times 8 \text{ mm}$ with a height of 2.3 mm , as shown in Figure 6.17 (c). EDX mapping was used to visualise material distribution, with Sn highlighted in green and In in red. Minor signal noise and mixing, likely due to subsurface reflections, were observed. Nonetheless, the structure exhibited no signs of collapse, unintended material bridging, or irregular droplet deposition. The overall geometry remained stable and consistent.

The average gap widths between Sn-In and In-Sn finger pairs were measured at $133 \pm 1 \mu\text{m}$ and $141 \pm 1 \mu\text{m}$, respectively. In such interdigitated or grating structures, alignment error along the finger axis (E_X) can be quantified by the difference between these two gap values, which is:

$$E_X = \frac{1}{2} |w_2 - w_1| \quad (6.1)$$

Where w_1 is the width of the Sn-In gap and w_2 is the width of the In-Sn gap. e_X is calculated as $3.68 \mu\text{m}$, which is an acceptable value.

Table 6.2 Gap width measurements (μm) of the interdigitated structure

	1	2	3	4	5	Average
Sn-In gap	133.85	132.25	132.76	133.28	134.68	133.64
In-Sn gap	141.21	142.05	140.31	141.36	141.73	141.33

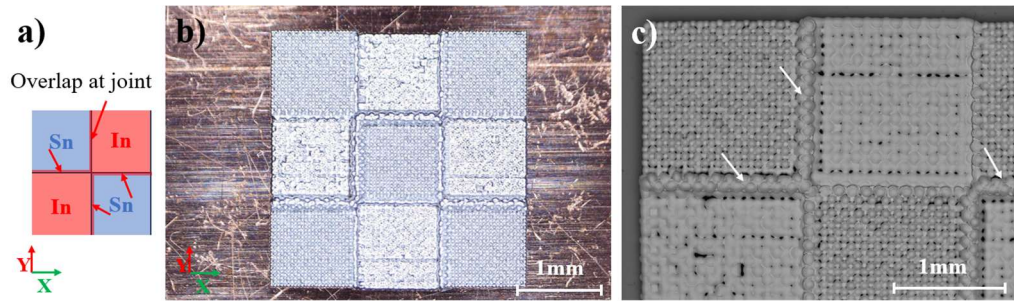


Figure 6.17 A multi-material interdigitated structure printed with Sn and In at $T_s = 60^\circ\text{C}$. (a) Photograph of the sample (b) Camera image top view (c) EDX mapping on the SEM images at vertical fingers (d) SEM image and measurement at fingers

6.4 Summary of multi-material printing

This chapter investigated the composition, formation mechanisms, and potential defects at the interface between dissimilar materials to develop a printing strategy capable of enabling seamless multi-material MMJ fabrication. FIB-SEM analysis of droplet-by-droplet sample cross-sections revealed that the interface comprises In-rich β phases and Sn-rich $\beta + \gamma$ phases. A key observation was that subsequently deposited droplets tended to coalesce towards the previously solidified dissimilar material, often creating a gap for following droplets. This phenomenon of droplet coalescence at dissimilar metal interfaces has not previously been reported in the MMJ field, as multi-material jetting has not yet been systematically explored.

Importantly, this study is the first to identify and explain the physical mechanism behind this issue, linking it to interfacial phase formation and solidification dynamics. Different from the existing single-material MMJ studies, where process optimisation can be finished by adjusting printing parameters, here the coalescence effect can not be mitigated even when the substrate temperature was reduced to its lower limit of 60 °C. By modifying the deposition sequence and material ratio, the issue was mitigated, leading to the development of a novel “Squeezed-Alternate” printing strategy. This approach demonstrates an effective and repeatable method for eliminating interfacial gaps and achieving seamless integration of dissimilar metals in MMJ. In doing so, this work extends MMJ from its previous limitation to single-material applications and provides a framework for designing future strategies in multi-material jetting.

7 Conclusions

This section includes the conclusions of three main result chapters: system development, printing strategies study and multi-material study.

7.1 Conclusion in system development

Throughout the system development phase, extensive details were provided on the design and implementation process of the control software tailored specifically for the MetalJet system. This software is engineered to maximise operational convenience while ensuring efficient and high-precision printing capabilities. It is important to note that system development is an ongoing process of enhancement, necessitating future upgrades in software, hardware, and experimental methods to keep pace with technological advancements and user requirements.

Initial experiments utilising Sn and Ag were conducted to assess the dual-head MetalJet system's printing capabilities at varying nozzle temperatures. Various test patterns were printed and subsequently analysed to evaluate print quality. Key findings from the system development and evaluation include:

1. The development of the Dual-head MetalJet system was proved to be successful via initialise experiments.
2. The system's capability to handle multiple materials is verified by Sn initialise printing and Ag initialise printing.
3. The printing of Sn-Sn checkerboard patterns exhibited an alignment error within 7 μm , which showed acceptable levels of overlap at junctions, thus validating the efficacy of the printhead alignment process.

The system development presented in this thesis provided a thorough evaluation of the dual-head printer's capabilities and showcased the adaptability of the custom software for multi-material printing. These contributions established a robust technical foundation for the subsequent experimental studies and marked the establishment of the world's first multi-material MMJ printer.

7.2 Conclusion of printing strategies

Aimed to directly print functional components with improved properties, the printing strategy development section created three novel deposition strategies in MMJ, namely Staggering, Honeycomb and Alternate. By comparing these strategies with the conventional Normal method, we evaluated the density, electrical conductivity, and surface roughness (R_a) of samples printed with Sn at three different substrate temperatures. The key findings are:

1. At both high and medium substrate temperatures, the Staggering, Honeycomb, and Alternate strategies were effective in producing fully dense parts (with density of $99.67\pm0.05\%$, $99.73\pm0.05\%$ and $99.11\pm0.05\%$, respectively), unlike the Normal strategy (which achieved only $98.01\pm0.05\%$).
2. For high and medium temperatures, Staggering and Honeycomb strategies resulted in smoother surfaces (with R_a values of $4.41\mu\text{m}$ and $4.94\mu\text{m}$, respectively) compared to Normal and Alternate (R_a values of $5.50\mu\text{m}$ and $5.80\mu\text{m}$, respectively).
3. At high and medium temperatures, Staggering, Honeycomb, and Alternate strategies achieved electrical conductivity levels with only 1% to 1.5% gap to that of bulk Sn.
4. Among the strategies applied at high and medium substrate temperatures, Staggering and Honeycomb strategies were found to be the most suitable overall, balancing part density, electrical conductivity and surface roughness.
5. At low substrate temperatures, the Normal, Staggering, and Honeycomb strategies exhibited varying degrees of delamination, with the Alternate strategy proving to be the only viable option.
6. The density of samples printed using the Alternate strategy showed a decrease as the substrate temperature lowered. However, even at the lowest temperature, the density achieved with the Alternate strategy remained higher than that obtained with the Normal strategy at high temperatures.

The printing strategy section offers valuable insights into enhancing density, electrical conductivity, and surface quality in the MMJ process. These findings guided the selection of the most appropriate deposition strategy based on specific process requirements and desired final part characteristics.

7.3 Conclusion of multi-material printing

This study investigated the formation of the Sn-In interface during multi-material MMJ printing to identify optimal process parameters and printing strategies for achieving high-quality, seamless deposition. Experimental samples were produced by printing Sn and In droplets 40 μm apart in arrays. The resulting microstructures and elemental distributions were examined through cross-sectional analysis using EDX and FIB-SEM. The influence of substrate temperature, deposition sequence, and deposition ratio was evaluated. To address challenges associated with droplet coalescence and to enable defect-free multi-material builds, two printing strategies were developed and evaluated: the Slicing strategy and the Squeezed-Alternate strategy.

The key findings of this investigation are summarised as follows:

1. Metallurgical bonding was consistently observed at the Sn-In interfaces across all tested substrate temperatures (60°C to 100°C) and deposition sequences (Sn-first-In-second and In-first-Sn-second). No pores or cracks were detected, indicating reliable interfacial integrity under varied conditions.
2. The interface comprises a Sn-rich region and an In-rich region. Elemental analysis revealed that the Sn-rich area consists primarily of the γ phase (71% - 80% Sn and 20% - 29% In), while the In-rich region contains a $\beta + \gamma$ phase (36% - 41% Sn and 59% to 64% In).
3. A three-stage mechanism is proposed for interface formation: (i) initial remelting at the contact region, (ii) interdiffusion of molten Sn and In before solidification, and (iii) phase segregation during solidification, which determines the final microstructure.
4. During deposition, the second droplet was observed to partially coalesce with the first, previously solidified droplet. This is attributed to differences

in surface tension between droplet–droplet and droplet–substrate interfaces. Such coalescence may result in positional gaps for subsequent droplets.

5. Though the phase segregation line shifts towards the In-rich side when reducing the substrate temperature from 100°C to 60°C, coalescence cannot be prevented.
6. Coalescence was reduced by using an appropriate deposition sequence, specifically the In-first-Sn-second sequence.
7. Introducing a dissimilar droplet between two identical ones was found to significantly suppress coalescence effects, contributing to improved uniformity for subsequent droplets
8. The Squeezed-Alternate strategy proved highly effective in mitigating errors caused by coalescence between dissimilar droplets. It also demonstrated resilience to variations in jetting trajectory and droplet size. As a result, this strategy has been selected for future multi-material printing.

This chapter presented a detailed characterisation of the Sn-In interface composition and offered a reliable hypothesis for its formation mechanism. An innovative multi-material printing strategy was developed to address the challenge of droplet coalescence between dissimilar materials, enabling the reliable fabrication of seamless multi-material structures. The result showed the guiding significance of other material pairs in multi-material MMJ printing.

8 Future work

This doctoral thesis has established the foundational work in developing a system for multi-material MMJ printing, marking the first exploration into this area. It has successfully demonstrated the feasibility of the MMJ process for multi-material applications, providing initial insights into interface formation and the influence of printing parameters on multi-metal printing. However, to transition MMJ into a mainstream industrial application, substantial research is still necessary. Future efforts will concentrate on several key areas:

In-depth exploration of interface formation mechanisms

Future studies will aim to understand more comprehensively the mechanisms governing the formation of interfaces between different metals. This involves developing a numerical simulation model that accurately describes the interface dynamics, factoring in the changing concentrations and temperatures during the process. This model should incorporate aspects such as droplet displacement due to remelting and coalescence, and composition changes due to interdiffusion, representing a novel and challenging topic in MMJ research.

Optimisation of printing parameters and strategies

Although initial studies indicate that substrate temperature and droplet temperature have a limited effect on droplet coalescence, the impact of other parameters has yet to be fully explored. Moreover, innovative printing strategies that could mitigate issues like droplet coalescence need development. This includes further lowering the T_s value to room temperature. Applying a special printing strategy can be another way to achieve the process optimisation.

Joining of high melting point materials

The initial experiments utilised Sn and In due to their low melting points and simple binary phase diagrams, which facilitated the experimental setup. Future work should explore materials with higher melting points and more complex compositions, such as copper and silver or functional alloys. This could expand the application possibilities for MMJ technology beyond the current limitations imposed by simpler materials.

Advanced Toolpath Planning

The current raster-based toolpath planning method, borrowed from Inkjet technology, is not ideally suited for the single-nozzle MMJ process due to its inefficiency and precision loss, particularly when printing oblique lines or arcs. Future developments should focus on a hybrid toolpath strategy that combines raster-based methods for filling large areas with vector-based paths for contours and detailed features. This approach would better utilise the capabilities of MMJ hardware, particularly the robust FPGA setup, to enhance both the efficiency and accuracy of the printing process. Currently, after revisions on the control software, a simple verification of a tile line has been printed to prove that vector-based printing on the MetalJet setup is accessible.

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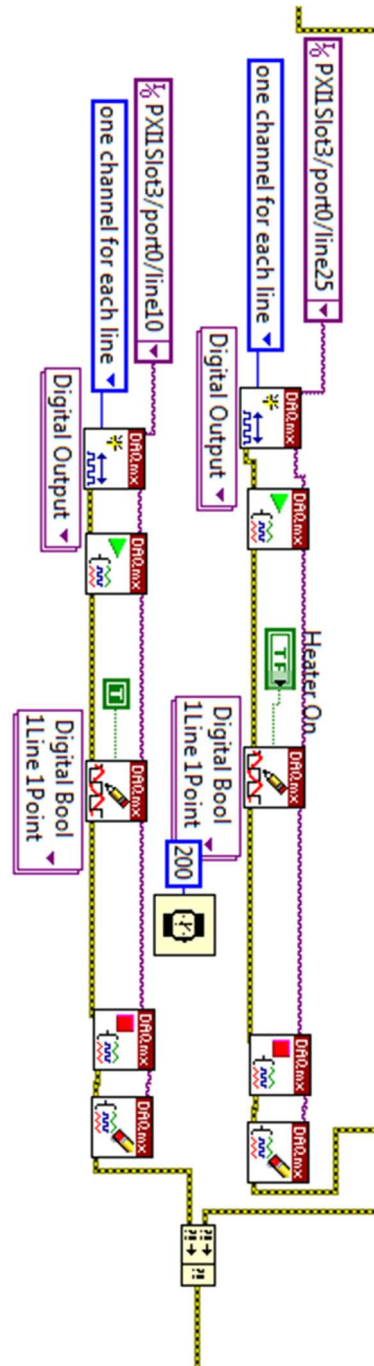
Electronics, vol. 28, no. 21, pp. 16120–16132, Nov. 2017, doi: 10.1007/s10854-017-7512-3.

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Appendix 1: LabVIEW coding for each key device

Substrate Heating

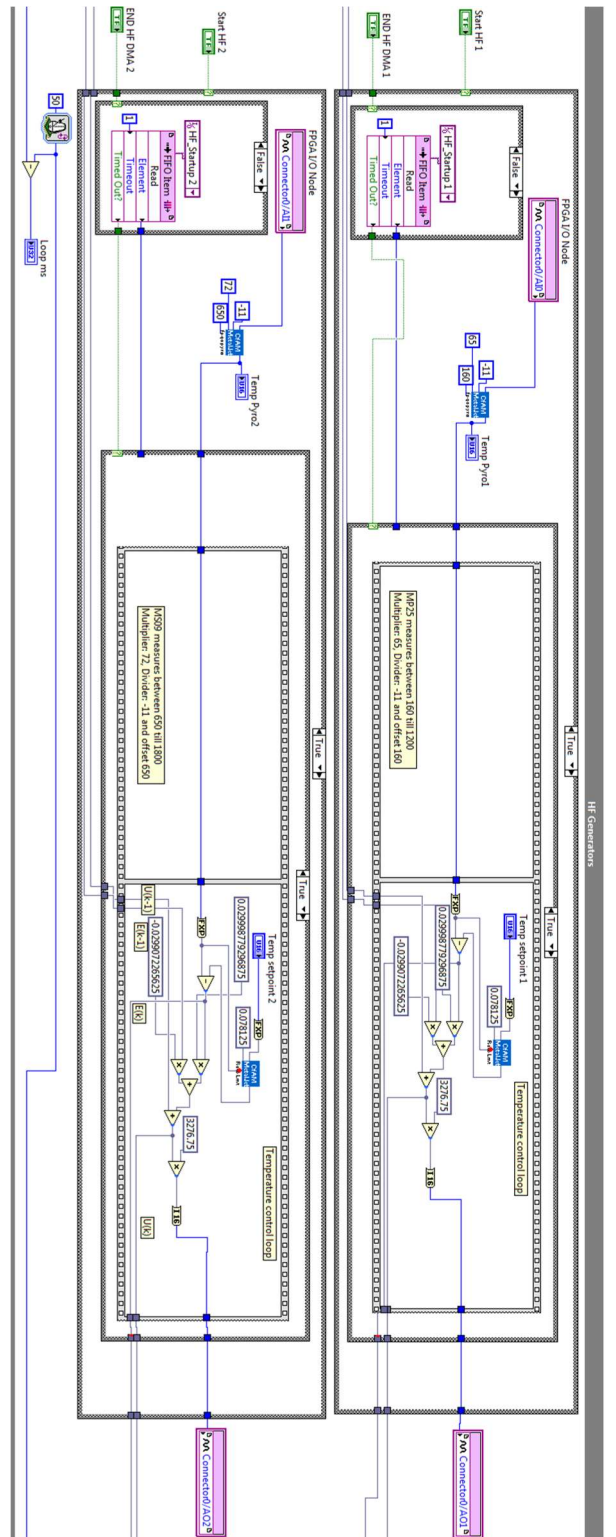
Substrate heating involves direct control of the heater using port control APIs, as shown in Appendix Figure 1



Appendix Figure 1 LabVIEW code for substrate heating

Induction Heating PID control (FPGA embedded)

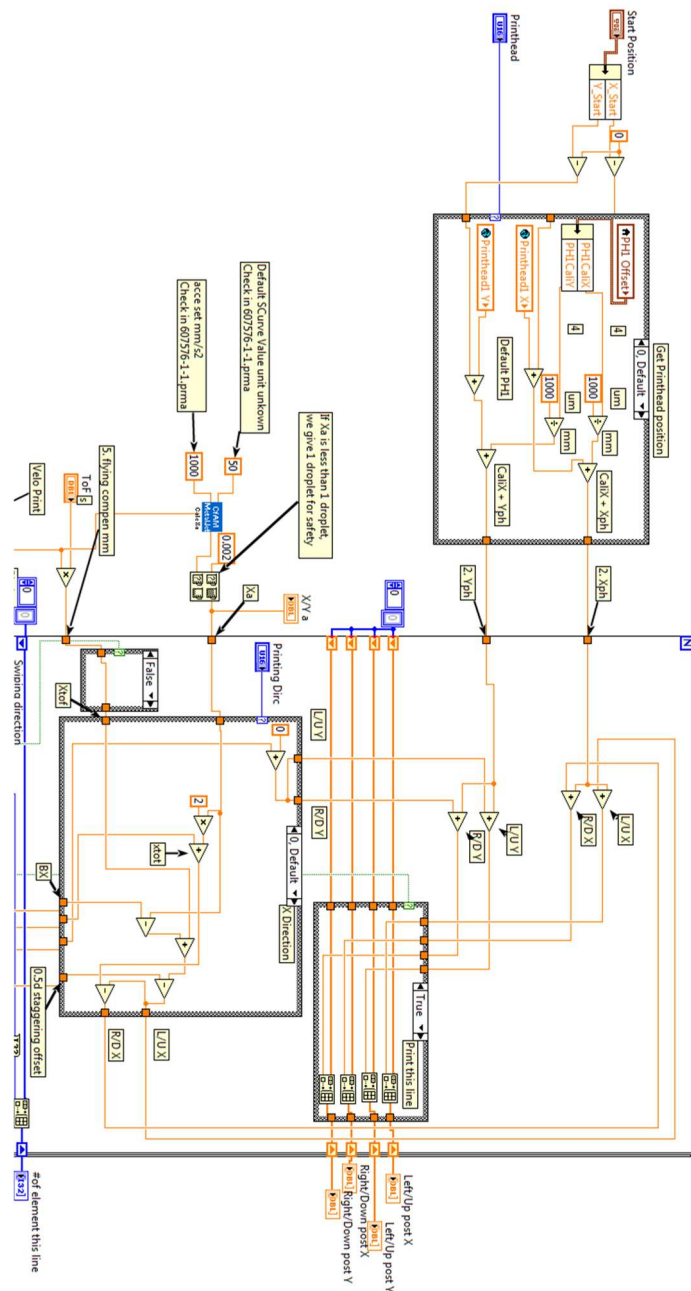
The nozzle temperature control involves an analogue reading input from the pyrometer and an analogue output to the HF generator with PID control, as shown in Appendix Figure 2.



Appendix Figure 2. PID temperature control to the FPGA

Bitmap transfer to droplet position (toolpath planning)

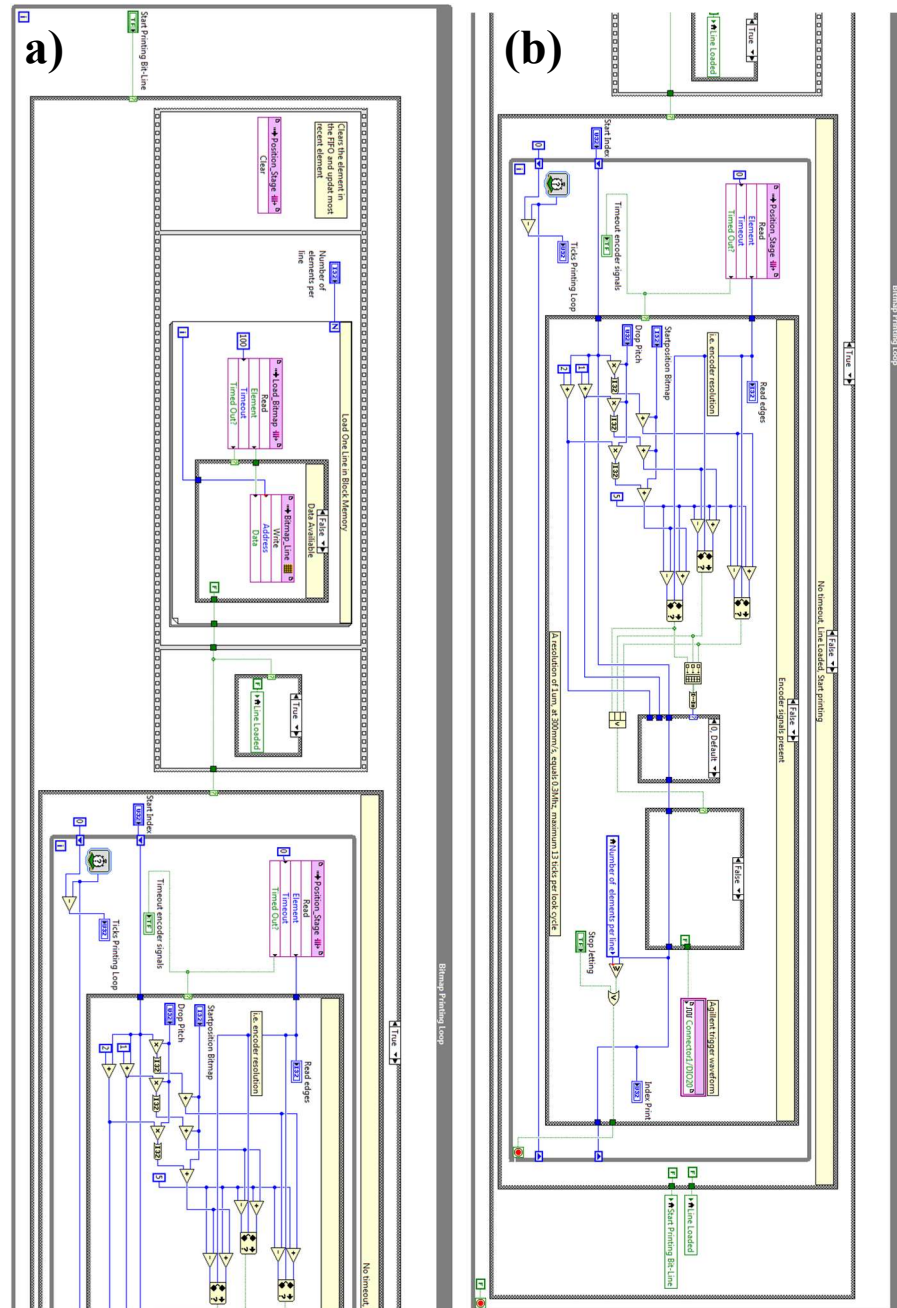
This function acts as our raster-based toolpath planning module. It maps each pixel in the bitmap to the desired position of the individual droplet. The array index of the pixel is multiplied by the ds to know the line length, start point and end point. Empty droplets and beginning and ends were cut away in this process. Additionally, the toolpath length, start point and end point need to consider the acceleration and deceleration distance. These relative positions were then added to the coordinate of the printhead to get the raster toolpath.



Appendix Figure 3. Raster toolpath planning with “head” and “tail” cropped

Jetting triggered by encoder reading (FPGA embedded)

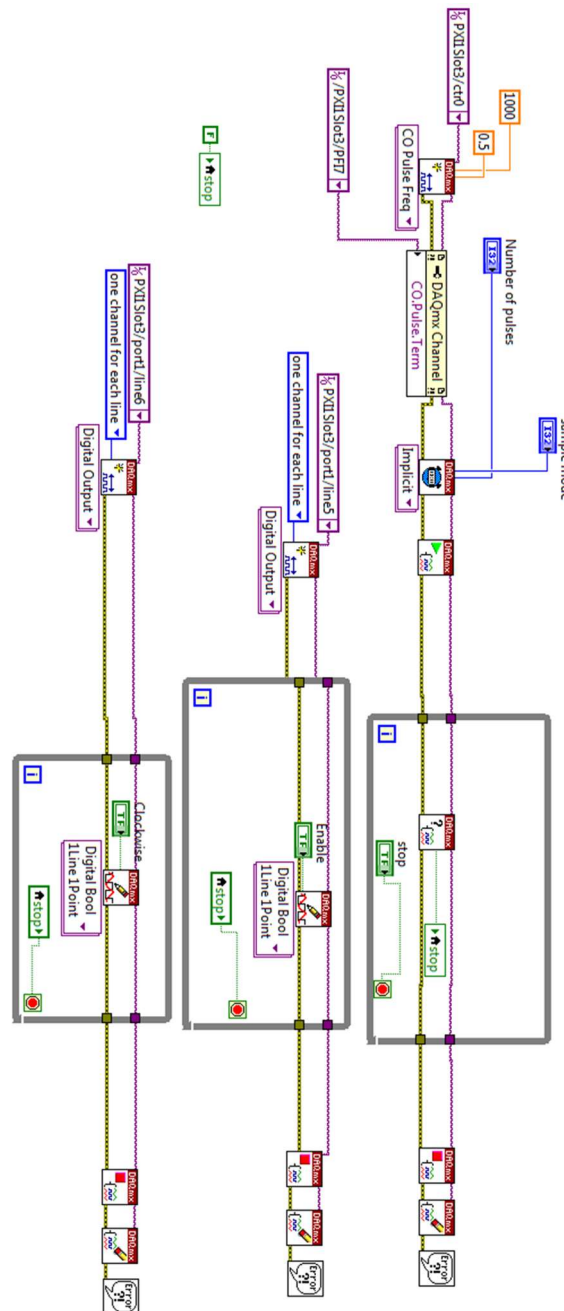
This function is the printing actuation part of the programme. The FPGA reads the encoder pitch from the linear stages and knows the index of the droplet position it arrives at. In the meantime, the bool data processed from the toolpath planning is compared to the index and an actuation pulse is sent to the waveform generator when the bool data of the pixel is false, as shown in Appendix Figure 4.



Appendix Figure 4. Jetting trigger module in FPGA (a) reading encoder and stored in the data buffer (b) decoding the data and determines the jetting triggering signal

Motor moves for the LED strobe light

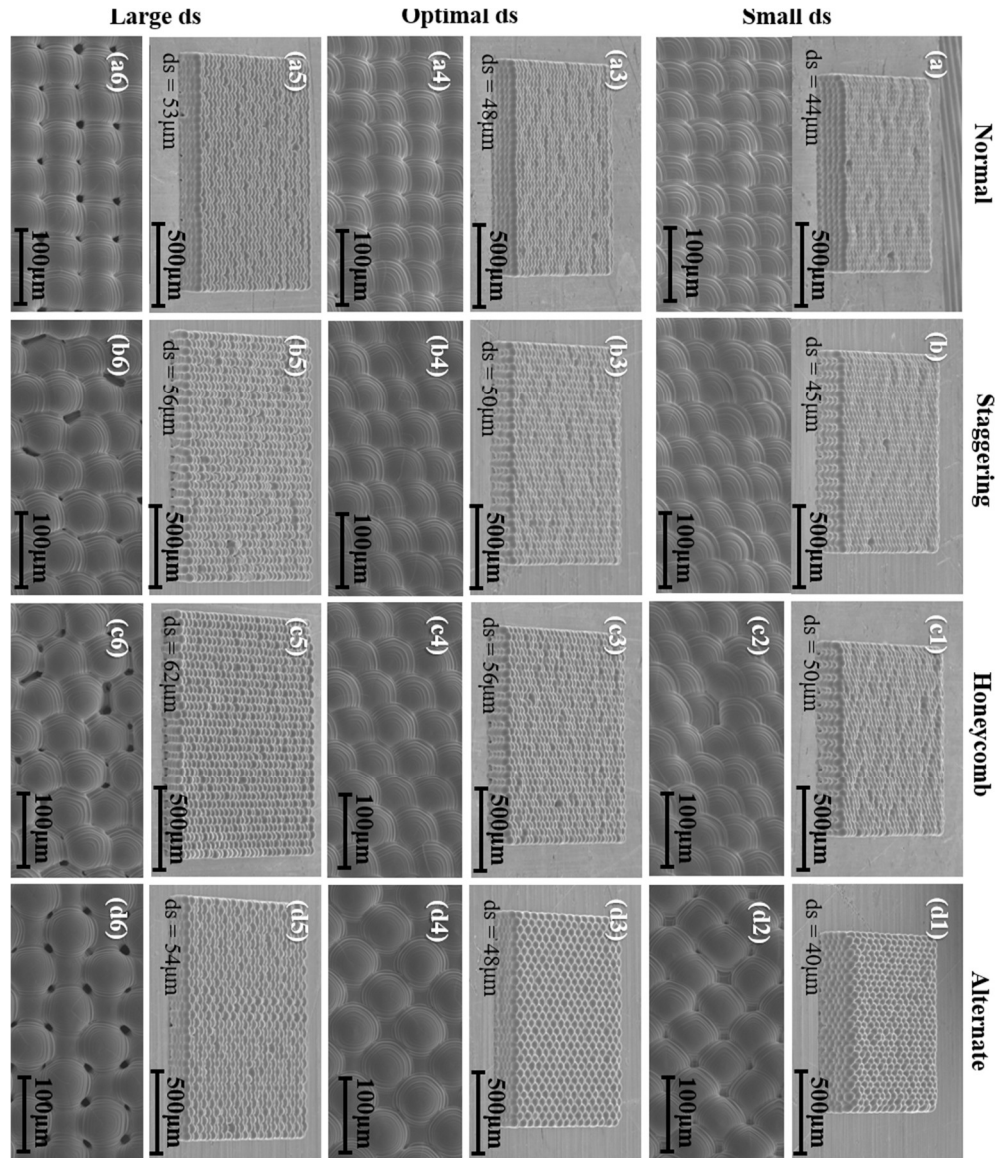
The stepper motor is connected to the LabVIEW Data Acquisition (DAQ) module and is driven by a number of pulses. Each pulse sent represents one pitch on the motor. The digital write pin is used to send these pulses. The pin is first set up in the software, and the signal frequency is defined. As the stepper motor uses an open-loop control, moving it to the destination with high accuracy is impossible. In this way, a jog function is needed to make the stepper motor move pitch by pitch, compensating for the position error to the desired position.



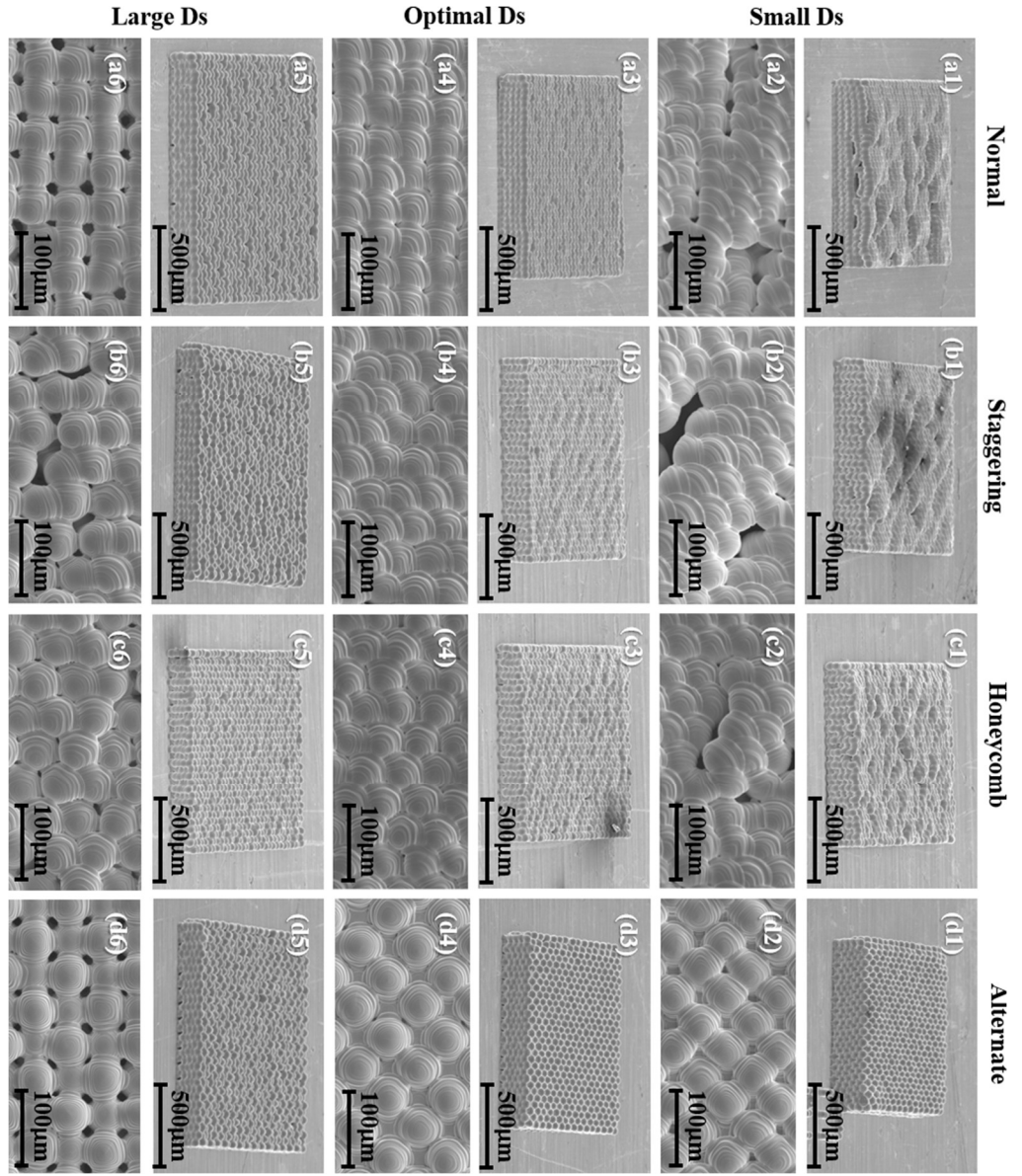
Appendix Figure 5. LabVIEW software (part) for stepper motor control

Appendix 2: SEM images of optimal droplet spacing calibration

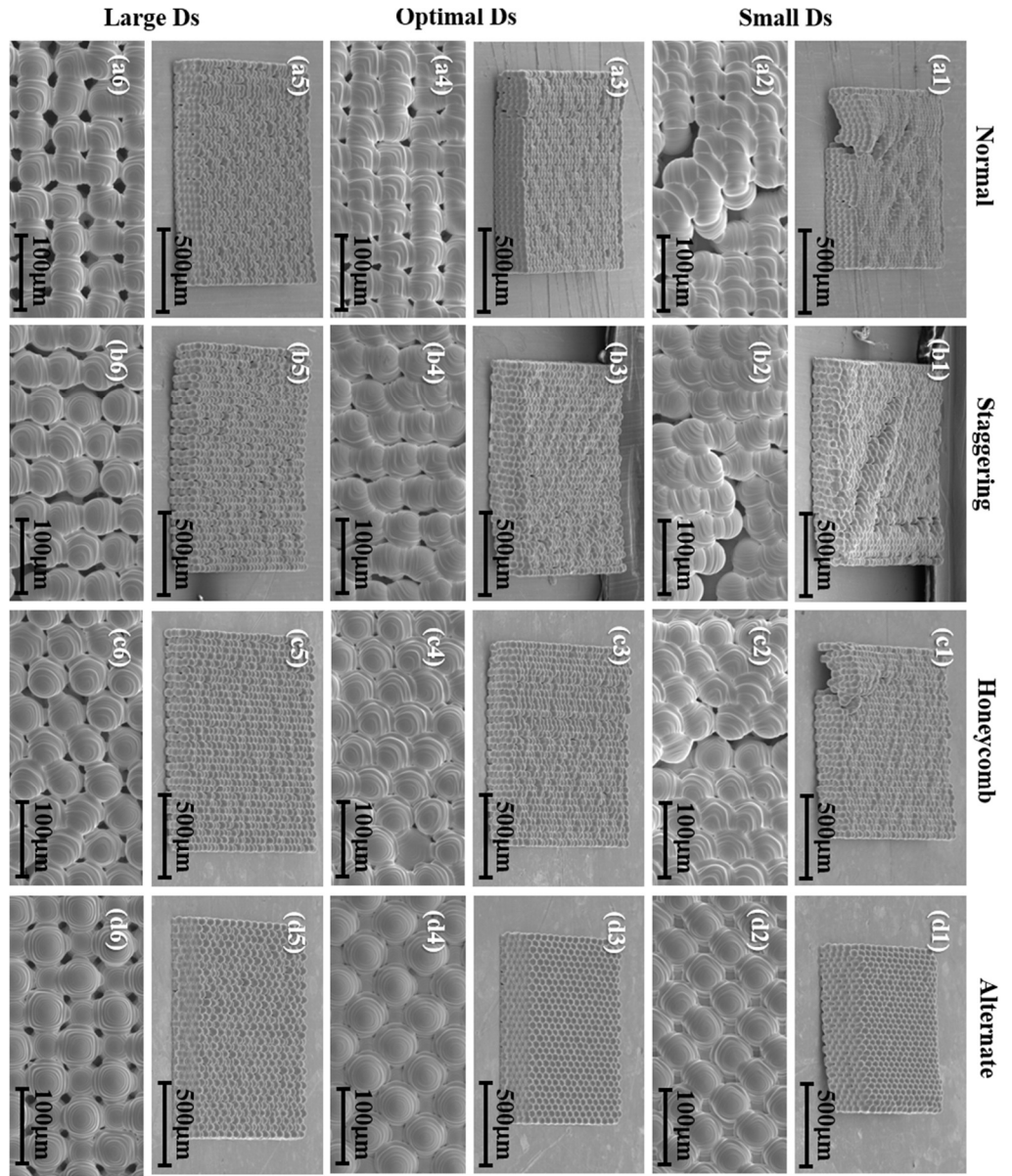
Appendix Figure 6, Appendix Figure 7, and Appendix Figure 8 show the images of a part of the samples fabricated at $T_s = 150^\circ\text{C}$, 100°C and 50°C during the calibration procedure. Here we define the ds smaller than the optimal value as “Small ds ”, while ds larger than the optimal value as “large ds ”. Four strategies are displayed from left to right in the sequence of Normal, Staggering, Honeycomb and Alternate. From top to bottom are the 3D view and x800 magnified view of samples printed at small, optimal and large ds of each strategy.



Appendix Figure 6. SEM images of ds_{opt} calibration samples, printed using Sn at $T_s=150^\circ\text{C}$.



Appendix Figure 7. SEM images of ds_{opt} calibration samples, printed using Sn at $T_s=100^\circ\text{C}$.



Appendix Figure 8. SEM images of ds_{opt} calibration samples, printed using Sn at $T_s=50^\circ\text{C}$.