

Elucidating the Effect of Sintering Time on the Process-Structure-Property Relationship of Inconel 625 Produced by Metal Extrusion Additive Manufacturing

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

Chapters 5 and 6 of this thesis are adapted from a journal article submitted to “Materials Science and Engineering: A” in April 2025, titled “Elucidating the Effect of Sintering Time on the Process-Structure-Property Relationship of Inconel 625 Produced by Metal Extrusion Additive Manufacturing.” The article was co-authored by the candidate, Dr. Sahil Rohila, Sajad Hosseinimehr, David Ester (industrial partner), and my supervisor, Prof. Michael Benoit.

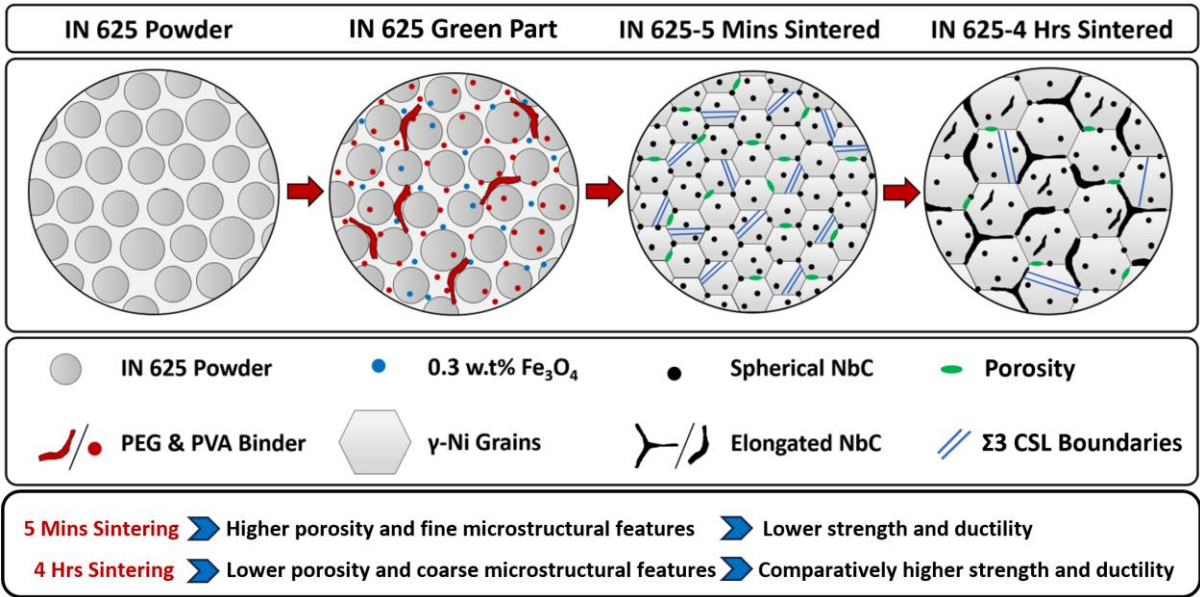
In this work, the candidate was primarily responsible for the characterisation, data analysis, and manuscript writing. Dr. Sahil Rohila conducted the sample fabrication via metal extrusion additive manufacturing. Sajad Hosseinimehr assisted with tensile testing, while David Ester provided guidance on the initial printing parameters. Prof. Michael Benoit supervised the project and contributed to the review and editing of the manuscript and also secured funding.

Abstract

Inconel 625 (IN625), a Ni-based superalloy valued for its strength and corrosion resistance, is known to suffer from microcracking during fusion-based additive manufacturing. Metal Extrusion Additive Manufacturing (MEAM) offers a solid-state alternative that eliminates solidification, thereby reducing the risk of microcracking. However, there is currently a lack of understanding between the interrelationship of process conditions, microstructure, and mechanical properties for IN625 produced by MEAM.

This study investigates the influence of sintering time, 5 mins (short time) versus 4 hrs (long time) at 1290 °C, on the densification, microstructure, and mechanical performance of MEAM-processed IN 625. The 4 hrs sintered sample achieved a higher relative density (99.5%) compared to the 5 mins sample (98.5%), and both developed (Nb+Mo) rich carbides with distinct morphologies and volume fractions. Extended sintering reduced residual porosity, resulting in improved tensile strength and elongation. Fractographic analysis confirmed ductile failure via microvoid coalescence in both cases. These findings underscore the critical role of sintering duration in optimising density; despite developing microstructure characteristics that should degrade mechanical properties at longer sintering times, the mechanical properties of the 4 hrs sample were superior to those of the 5 min sample, revealing reduction of porosity to be the critical mechanism for maximising mechanical properties for this alloy and process.

Graphical Abstract



Acknowledgments

First and foremost, I would like to express my deepest gratitude to my supervisor, Prof. Michael Benoit, for his unwavering support and guidance throughout my studies. His commitment to meeting with me regularly, even amidst his many responsibilities, has been invaluable. I am especially thankful for the many opportunities he provided me during my degree, including coordinating the MSAM and CAMJ seminars and serving as a course instructor under his mentorship. His patience, composure, and consistent encouragement, particularly during some unexpected challenges, have been truly admirable. I am sincerely grateful for his mentorship, which has greatly contributed to my growth and deepened my passion for research.

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Dedication

I dedicate this thesis to my loving parents, whose unwavering support, sacrifices, and encouragement have shaped the person I am today. To my father, for teaching me the value of hard work and determination, and to my mother, for her endless patience and belief in me. I also dedicate this work to my brother, whose constant support and guidance have been instrumental in every step of my learning journey.

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Chapter 1

1. Introduction

1.1 Additive Manufacturing

Additive Manufacturing (AM), commonly referred to as 3D printing, is a approach to fabricating three-dimensional components by sequentially adding material layer by layer, directly from a digital design. Unlike traditional subtractive manufacturing processes, which involve removing material from a bulk workpiece through machining, cutting, or milling, AM builds components by placing material only where material is needed [1, 2]. This fundamental shift enables the creation of complex geometries, reduced material waste, and the possibility of on-demand, localised production [3-5].

1.2 AM Process Workflow

The general AM production workflow is shown schematically in Fig. 1.1. The process begins with a digital model, typically generated through computer-aided design (CAD) or reverse engineering methods such as 3D scanning. The model is then sliced into thin cross-sectional layers by specialised software. These slices guide the AM machine in depositing material (metal, polymer, ceramic, or composite) layer by layer until the final part is formed. Depending on the AM technique, material may be deposited in the form of filament, powder, resin, or wire and may require thermal or chemical activation to solidify [2]. Such a sort of additive deposition of materials has shown tremendous growth and applications across sectors, including aerospace, automotive, biomedical, defence, and energy, where design flexibility, weight reduction, and rapid prototyping are critical [2,6].

Beyond its technical advantages, AM is increasingly recognised as a key enabler of sustainable manufacturing practices. By minimising material usage, reducing supply chain complexity, and enabling design-for-functionality rather than manufacturability, AM aligns closely with emerging trends in circular economy and decentralised production [7].

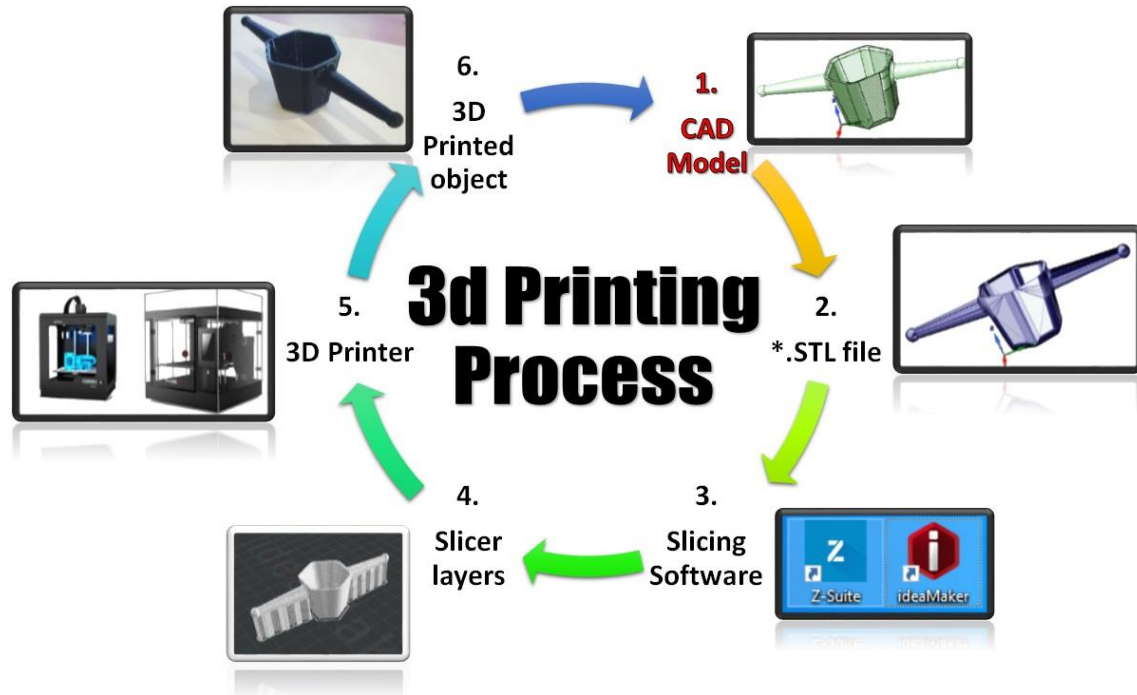


Fig. 1.1: Schematic representation of the 3D printing workflow. The process begins with the creation of a CAD model (Step 1), which is then exported as an STL file (Step 2). The file is processed using slicing software (Step 3) to generate layered instructions (Step 4) for the 3D printer. The instructions are executed by the 3D printer (Step 5), resulting in the fabrication of the final printed object (Step 6). This workflow illustrates the digital-to-physical transition fundamental to additive manufacturing [8].

As AM continues to mature, its integration into industrial manufacturing systems and research environments is shifting from prototyping to full-scale production [9]. Understanding this sequential process of AM is essential for exploring advanced topics such as microstructure-property relationships, defect control, and process optimisation. These are the areas that remain at the forefront of research in this rapidly evolving field [10].

1.3 Classification of AM Processes

Metal AM technologies are broadly classified into two principal categories: fusion-based and non-fusion-based (i.e., solid state) processes, depending on whether the material is melted during fabrication. As illustrated in the process hierarchy (Fig. 1.2), fusion-based processes, grouped under beam-based technologies, employ high-energy heat sources such as lasers, electron beams, and electric or plasma arcs to melt and solidify metal powders or wires. Common fusion-based methods include techniques like Laser Powder Bed Fusion (L-PBF), Electron Beam Melting (EBM), and Laser Directed Energy Deposition (L-DED), including trademarked processes such as Laser Engineered Net Shaping (LENS) and Laser Metal Deposition (LMD), and arc-DEC, often referred to as Wire Arc Additive Manufacturing (WAAM) [11]. These methods are capable of producing dense components with complex geometries and are widely adopted in aerospace, medical, and tooling applications where high structural integrity is critical [12].

Despite their advantages, fusion-based AM processes are associated with several inherent challenges. The rapid heating and cooling cycles involved in localised melting and solidification often lead to the formation of steep thermal gradients. These gradients can result in residual stresses, which increase the likelihood of solidification cracking and hot tearing, particularly in alloys with narrow solidification ranges or poor weldability. Additionally, the directional nature of heat dissipation promotes columnar grain growth along the build direction, which contributes to the development of strong crystallographic texture. This leads to anisotropic mechanical behaviour, where properties vary with orientation due to localised crystallographic texture evolution. Such anisotropy, coupled with microstructural inhomogeneities, can limit the reliability of components in structurally demanding applications [10].

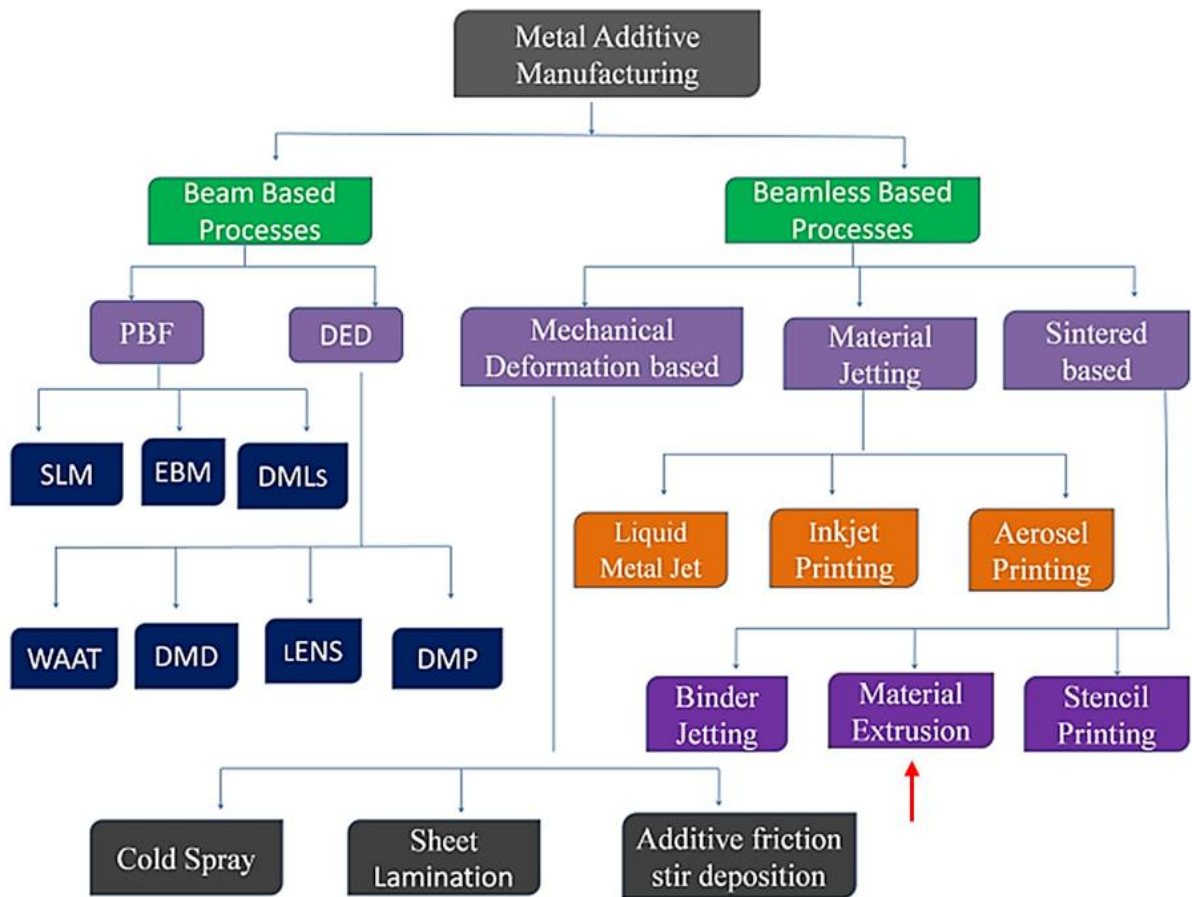


Fig. 1.2: Classification of Metal Additive Manufacturing (AM) processes. The diagram categorises AM techniques into two main groups: Beam-Based and Beamless-Based Processes [13].

In contrast, non-fusion-based or beamless AM processes fabricate components without inducing melting. These methods include mechanical deformation-based techniques (e.g., Cold Spray, Additive Friction Stir Deposition), material jetting approaches (e.g., Inkjet and Liquid Metal Jet), and sintering-based technologies (e.g., Binder Jetting, Material Extrusion) [14]. These beamless processes generally operate at lower temperatures, thereby minimising thermal stress, cracking risk, and distortion [15]. However, these benefits are often offset by lower initial part density and mechanical strength, necessitating post-processing steps such as sintering, infiltration, or hot isostatic pressing to meet functional performance requirements [13].

1.4 Thesis Outline

This thesis is composed of seven chapters in total. The first chapter provides an introduction to additive manufacturing and the different types of metal additive manufacturing. Chapter 2 presents a comprehensive overview of Ni-based superalloys, particularly Inconel alloys, including their microstructural aspects, advantages, and disadvantages when processed using fusion-based additive manufacturing technologies. It also covers the background and literature review of metal extrusion additive manufacturing. Chapter 3 outlines the motivation, identified literature gaps, and objectives of the present work. Chapter 4 describes the materials and methods used for characterizing powders, pastes, and sintered components, as well as their mechanical properties. Chapter 5 presents the experimental results, while Chapter 6 discusses and interprets these findings. Finally, Chapter 7 provides the conclusions and recommendations for future work.

Chapter 2

2. Literature Review

2.1 Introduction to Inconel 625 and Its Microstructural Aspects

Among the wide variety of nickel (Ni)-based superalloys, Inconel 625 has garnered substantial attention across multiple high-performance engineering sectors, including aerospace, aeronautical, marine, chemical processing, and petrochemical industries [16,17]. This widespread applicability stems from its exceptional combination of mechanical and chemical properties, which include high strength, outstanding oxidation and corrosion resistance, and superior performance under high-temperature, high-stress environments. Notably, the alloy also demonstrates excellent fatigue and creep resistance, in addition to good weldability and fabricability, making it particularly attractive for use in complex manufacturing processes, including welding and additive manufacturing [16,18].

Inconel 625 is primarily a solid solution-strengthened alloy, with its strength derived largely from the presence of niobium (Nb), molybdenum (Mo), and iron (Fe) in the nickel matrix. The chromium (Cr) and molybdenum (Mo) are typically added for corrosion resistance [19]. However, under certain thermal conditions, the alloy can exhibit precipitation of various secondary phases due to the presence of Nb, Ti and Al, which significantly influence its mechanical and metallurgical behaviour. At temperatures exceeding 850 °C, the precipitation of carbide phases such as MC, M₆C, and M₂₃C₆ (where M typically refers to Nb, Mo, or chromium (Cr)) is commonly observed [20]. These carbides typically form during solidification processes, such as casting and fusion-based additive manufacturing, and tend to segregate at grain boundaries, potentially affecting the alloy's toughness and creep properties. Fig. 2.1 (a & b) denote the TTT curves for Inconel 625 and show the formation of carbides at grain boundaries in casting. Furthermore, the formation of brittle intermetallic compounds,

most notably the Laves phase, a Nb- and Mo-rich constituent, is a critical concern during solidification. This phase is often found in the interdendritic regions following casting, welding, or laser-based additive manufacturing processes and is shown in Fig. 2.1 (c). The presence of such phases can lead to microstructural embrittlement and reduced ductility [21], thus necessitating careful control of processing parameters to minimise their formation.

Conversely, sub-850 °C heat treatments, commonly referred to as aging treatments, promote the precipitation of gamma prime (γ'), gamma double prime (γ''), and delta (δ) phases. Fig. 2.1 (d) shows the formation of γ' , γ'' and δ in the aged Inconel 625 samples. These fine, coherent or semi-coherent precipitates contribute significantly to strengthening the alloy by impeding dislocation motion, thereby enhancing both room-temperature and elevated-temperature mechanical performance [22]. While γ' and γ'' phases are more commonly associated with other superalloys like Inconel 718, controlled aging in Inconel 625 can also lead to limited but beneficial precipitation of strengthening phases under appropriate thermomechanical conditions [23].

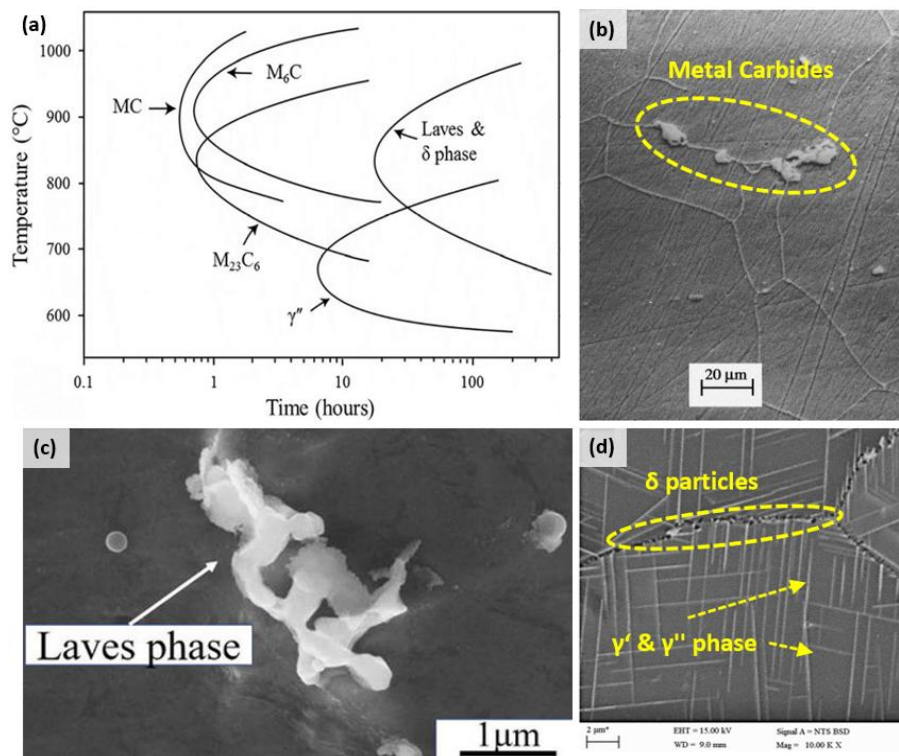


Fig. 2.1: (a) Time-Temperature-Transformation (TTT) diagram of Ni-based superalloys indicating precipitation and phase transformation behaviour [24], (b) Optical micrograph showing carbide precipitates located at grain boundaries [25], (c) Formation of Laves phase at the terminal stage of solidification, and (d) Backscattered electron (BSE) micrograph of Inconel 625 aged at 725 °C for 1000 hours, revealing microstructural evolution including precipitation [26].

2.2 Fusion-Based AM

Fusion-based additive manufacturing (AM) processes use localized melting of metal powders or wires via high-energy heat sources (laser, electron beam, or arc). Key processes include Laser Powder Bed Fusion (L-PBF), Electron Beam Melting (EBM), Directed Energy Deposition (DED), and Wire Arc AM (WAAM). Powder bed techniques (L-PBF, EBM) offer fine resolution, whereas deposition processes (DED, WAAM) enable higher deposition rates and larger builds. Fusion-based AM generally achieves near-full density, strong interlayer bonding, and allows processing of advanced alloys, but challenges include residual stresses, porosity, vaporization of alloying elements, and microcracking [27,28].

2.2.1 Microstructural Features of Fusion-Based AM

Fusion-based AM is characterized by rapid cooling rates (10^3 – 10^8 K/s) and steep thermal gradients, which produce hierarchical microstructures. Columnar grains aligned along the build direction dominate due to directional solidification, leading to strong crystallographic textures and mechanical anisotropy. Fine cellular substructures enriched with solute segregation form within grains as solutes are rejected at solidification fronts. These solute-enriched boundaries can persist even after moderate heat treatments, strengthening the alloy but reducing ductility [29–31].

Layer-by-layer thermal cycling can also induce precipitation of carbides or intermetallics, while residual oxygen, nitrogen, or hydrogen may further influence strength and ductility. The resulting multiscale hierarchy includes grains, cellular substructures, nano-precipitates, and atomic-scale impurities (Fig. 2.2), each contributing to strengthening [32,33].

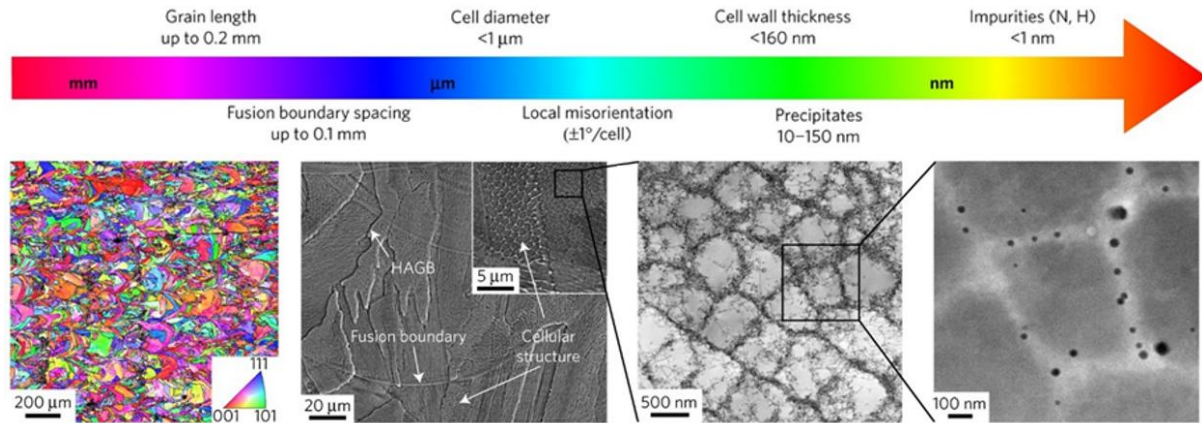


Fig. 2.2: Hierarchical microstructures intrinsic to fusion-based AM [32]

2.2.2 Challenges in Fusion-Based AM of Ni-Based Alloys

Although Ni-based superalloys are widely used in aerospace and power industries, their processing by fusion-based AM is difficult due to porosity, anisotropy, elemental evaporation, and cracking [34,35].

2.2.2.1 Porosity

Porosity arises from lack of fusion (LOF), keyhole instability, or gas entrapment. LOF defects occur under insufficient melting, typically appearing at track or layer interfaces (Fig. 2.3a). Keyhole porosity results from excessive energy input and melt pool instability (Fig. 2.3b). Gas porosity produces smaller spherical pores due to entrapped gas or powder contamination. Optimized process parameters and high-quality powders minimize porosity [34–39].

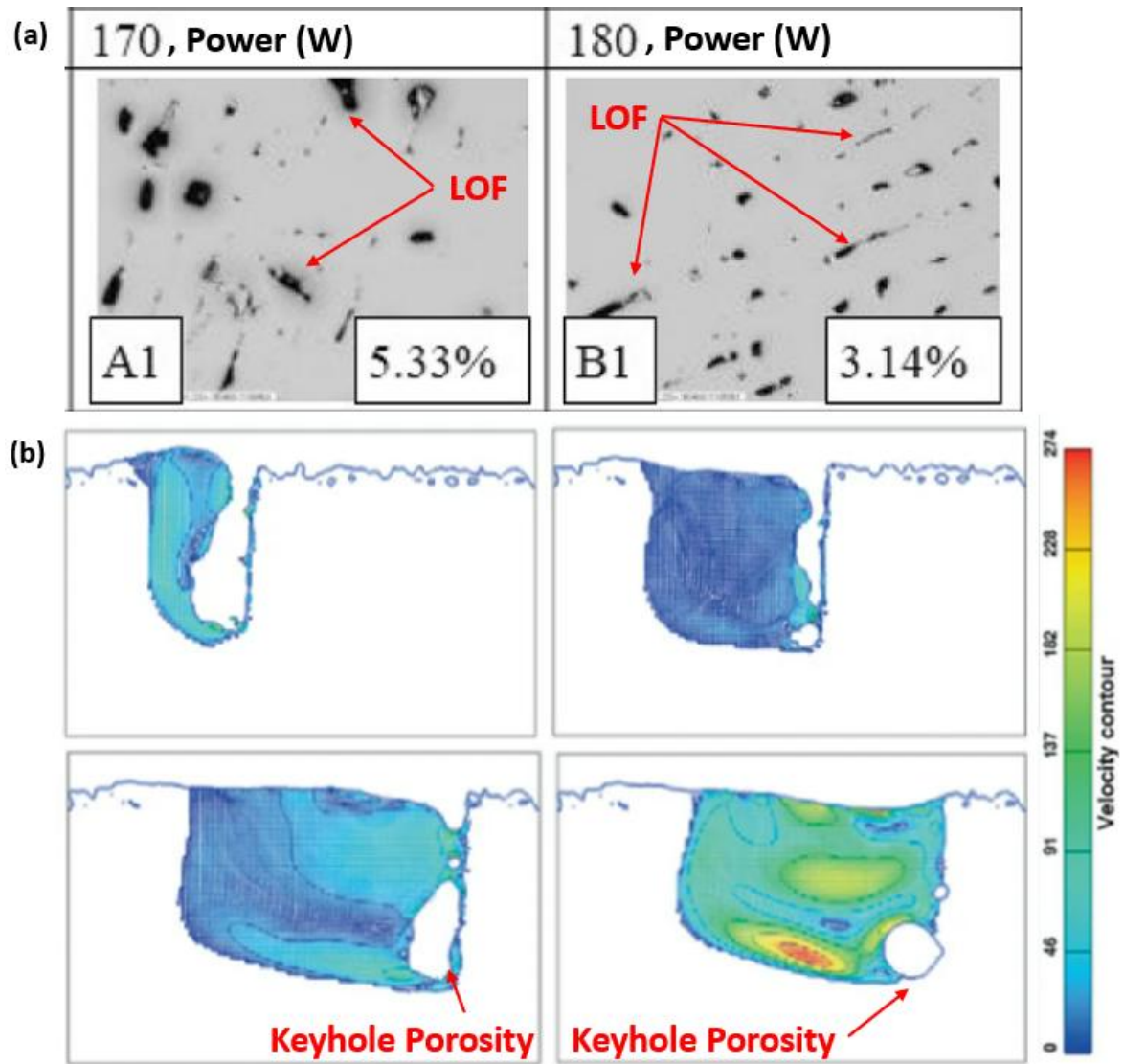


Fig. 2.3: (a) Lack of fusion (LOF) porosity in L-PBF Inconel 718 [38], and (b) Computational fluid dynamics (CFD) simulation of keyhole-induced porosity evolution in Inconel 718 during laser powder bed fusion (L-PBF) [39].

2.2.2.2 Anisotropy

Strong anisotropy results from epitaxial columnar grain growth along the build direction (Z-axis), producing elongated grains and $\langle 001 \rangle$ texture, while the XY-plane exhibits more equiaxed grains. This microstructural orientation leads to directional mechanical properties.

For instance, L-PBF parts often show higher strength in XY-plane specimens compared to Z-axis ones (Fig. 2.4). Heat treatments can reduce but not eliminate anisotropy [40–42].

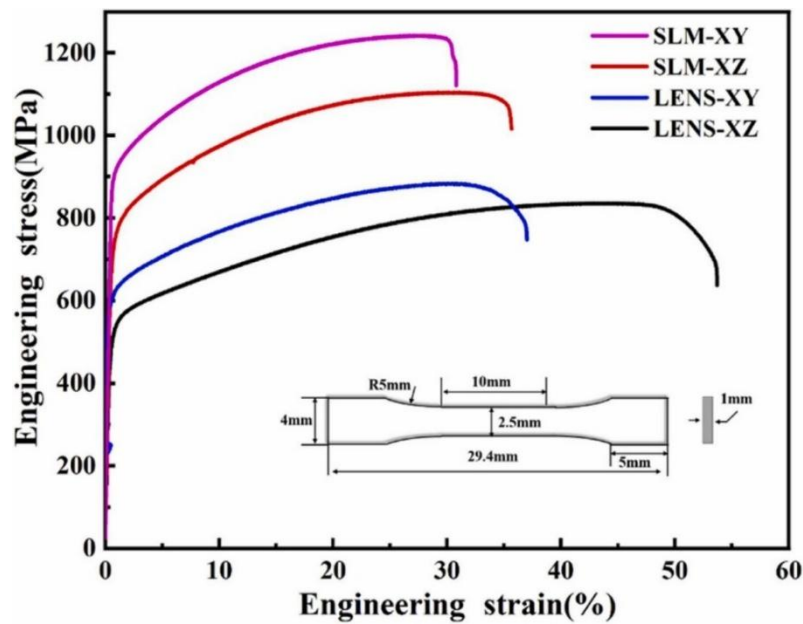


Fig. 2.4: Engineering stress-strain curves of Inconel 625 specimens fabricated via (L-PBF/SLM) and (L-DED/LENS), tested in the build direction (XZ plane) and the normal direction (XY plane) [42].

2.2.2.3 Loss of Alloying Elements

In EBM, high vacuum and high processing temperatures can vaporize volatile alloying elements (Al, Cr, Ni), degrading oxidation resistance and altering γ' phase fractions. Elemental loss varies with power input, with chromium showing the highest volatility (Fig. 2.5). Powder degradation due to partial sintering further limits reusability, increasing costs and making EBM less studied compared to L-PBF or DED [43–45].

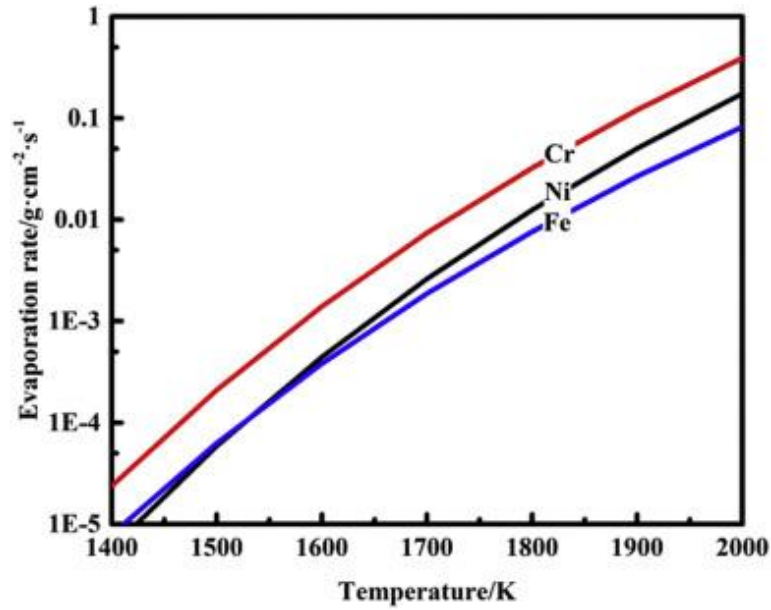


Fig. 2.5: Calculated evaporation rates of nickel (Ni), chromium (Cr), and iron (Fe) as a function of temperature, based on Langmuir's evaporation model. The plot illustrates the relative volatility of these alloying elements in Inconel 718 during high-temperature electron beam smelting (EDS) [45].

2.2.2.4 Cracking

Fusion-based AM of Ni-based alloys is prone to solidification and ductility-dip cracking. Rapid solidification promotes Nb/Mo segregation and brittle Laves phase formation at grain boundaries, which act as weak links under tensile stress. Repeated thermal cycling imposes high constraints, amplifying crack susceptibility. Although Inconel alloys are considered weldable, AM conditions can make cracking more severe compared to welding (Fig. 2.6).

Cracking tendencies vary across alloys and processes. Alloys such as Inconel 718 and 625 often exhibit solidification cracking linked to segregation and Laves phase formation, although in some cases cracking has not been reported, reflecting differences in alloy composition and processing parameters [46–49].

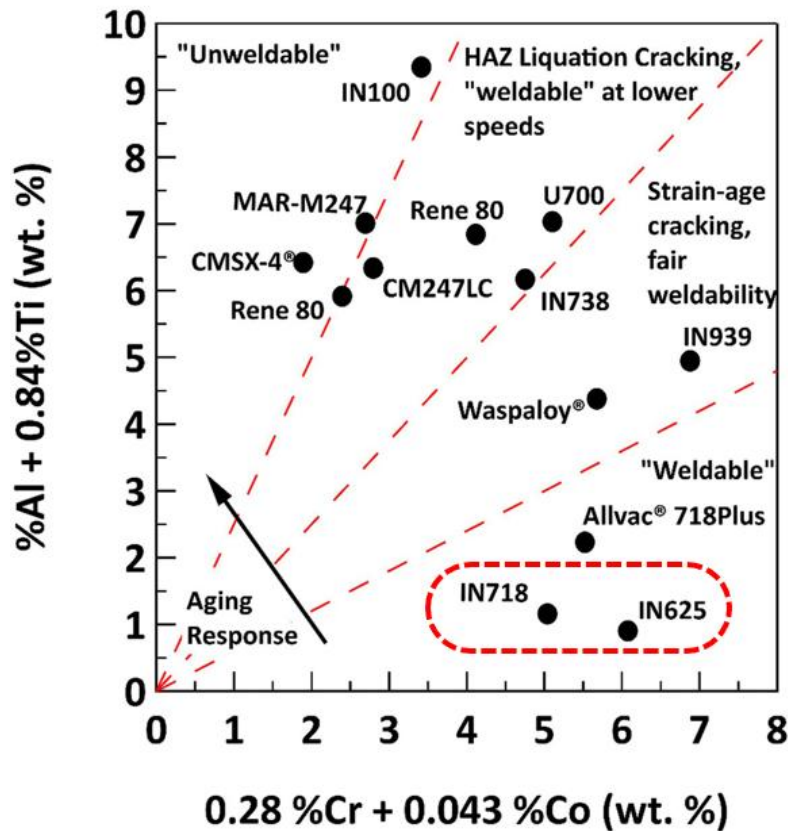


Fig. 2.6: Weldability chart of various nickel-based superalloys as a function of their chemical composition [46].

2.3 Solid State Additive Manufacturing (SSAM)

Due to the inherent and varied defects that can arise during fusion-based AM of Ni superalloys, solid state AM processes have emerged as an alternative printing method for these alloys. Solid State Additive Manufacturing (SSAM) refers to a class of additive manufacturing processes where material is joined and built up without melting. Unlike fusion-based methods, SSAM operates below the melting point of the material, relying on mechanisms such as frictional heat, plastic deformation or solid-state diffusion-based mechanisms to achieve fully dense, near-net shaped components [50].

Prominent Solid-State Additive Manufacturing techniques are [51]:

1. Friction Stir Additive Manufacturing (FSAM)

2. Cold Spray Additive Manufacturing (CSAM)
3. Binder Jetting (BJ)
4. Metal Extrusion Additive Manufacturing (MEAM)

FSAM employs severe plastic deformation and frictional heat to bond materials in the solid state, resulting in fine-grain structures. However, it is limited by its inability to produce complex or near-net-shape parts and generally requires substantial post-machining [52]. Similarly, Cold Spray relies on high-velocity particle impact for layer deposition, making it ideal for surface coatings and repairs, but impractical for geometrically complex parts due to its poor shape fidelity and the need for machining to reach final dimensions[51].

Binder Jetting, which selectively deposits a liquid binder onto a powder bed, allows for high-resolution, complex geometries. However, it suffers from several drawbacks, most notably, uneven binder wetting caused by poor flowability or interaction of the binder with the powder, which can lead to non-uniform densification after sintering. Additionally, loosely packed powders in this method can further exacerbate issues related to density gradients and strength variation due to excessive wetting of the binder on the powder [53]. In contrast, Metal Extrusion Additive Manufacturing (MEAM), which extrudes a metal-polymer composite filament/paste followed by debinding and sintering, offers a robust route to fabricate near-net-shape components. MEAM avoids the binder infiltration problems of Binder Jetting when dense powder compacts are used and eliminates the need for machining inherent to FSAM and Cold Spray.

While MEAM can present challenges with porosity and densification, these can be mitigated by optimising extrusion parameters, binder content, and implementing tailored sintering profiles. Owing to its ability to deliver high geometric accuracy and eliminate extensive post-processing, MEAM was chosen in this study for fabricating Inconel 625. This nickel-based

superalloy is highly prone to solidification cracking in fusion-based AM, making MEAM a promising alternative for achieving crack-free, structurally sound parts. The remainder of this sub-section focuses on the MEAM process fundamentals and the associated literature on issues that remain for the MEAM process [53].

2.3.1 Metal Extrusion Additive Manufacturing (MEAM) Process

Metal Extrusion-based Additive Manufacturing (MEAM) has gained significant traction in recent years as a promising solid-state or near-solid-state additive manufacturing technique. It is widely recognised for its cost-effectiveness, environmental sustainability, process versatility, and ability to fabricate complex geometries using a broad range of metallic materials. MEAM operates by extruding a feedstock material, typically in the form of a filament or paste composed of metallic powders and polymeric binders in a layer-by-layer fashion to build what is known as a ‘green part’. Although this green part maintains the intended geometry, it lacks the mechanical strength and density of a fully consolidated metallic component [54,55].

A key element in the MEAM process is the polymeric binder system, which plays a crucial role in maintaining the cohesion, printability, and mechanical stability of the feedstock during extrusion and deposition. Binders serve as a temporary supporting matrix, enabling the precise shaping of metal powder into a functional preform. Without binders, metallic powders cannot be extruded or formed reliably, as they do not possess the necessary structural integrity on their own [54,55].

Following printing, the green part undergoes thermal debinding and sintering, which are typically performed in a single continuous heat treatment cycle. During this cycle, the polymeric binder is gradually decomposed and volatilized (debinding phase), leaving behind a porous metal structure referred to as a ‘brown part’. As the temperature increases further in the same cycle, sintering occurs, during which atomic diffusion leads to densification, grain

bonding, and consolidation of the metallic particles, resulting in a strong, dense, and functional metallic component. The sequential processing from metal powders to fully densified parts in the metal extrusion-based additive manufacturing process is schematically depicted in Fig. 2.7. The illustration outlines each critical stage, beginning with the use of metal powders, followed by shaping through extrusion-based printing using a binder-containing feedstock, binder decomposition during thermal debinding, and final densification through sintering, resulting in a consolidated metallic component [56].

This integrated debinding–sintering approach not only simplifies the post-processing sequence but also minimises distortion and residual stress by providing a controlled thermal environment. Overall, the ability of MEAM to produce near-net-shape components with minimal thermal gradients and limited post-machining, combined with optimisation of printing parameters and sintering strategies to mitigate porosity, makes it an attractive method for manufacturing complex components from alloys like Inconel 625, which are otherwise prone to cracking in fusion-based AM processes [53,56].

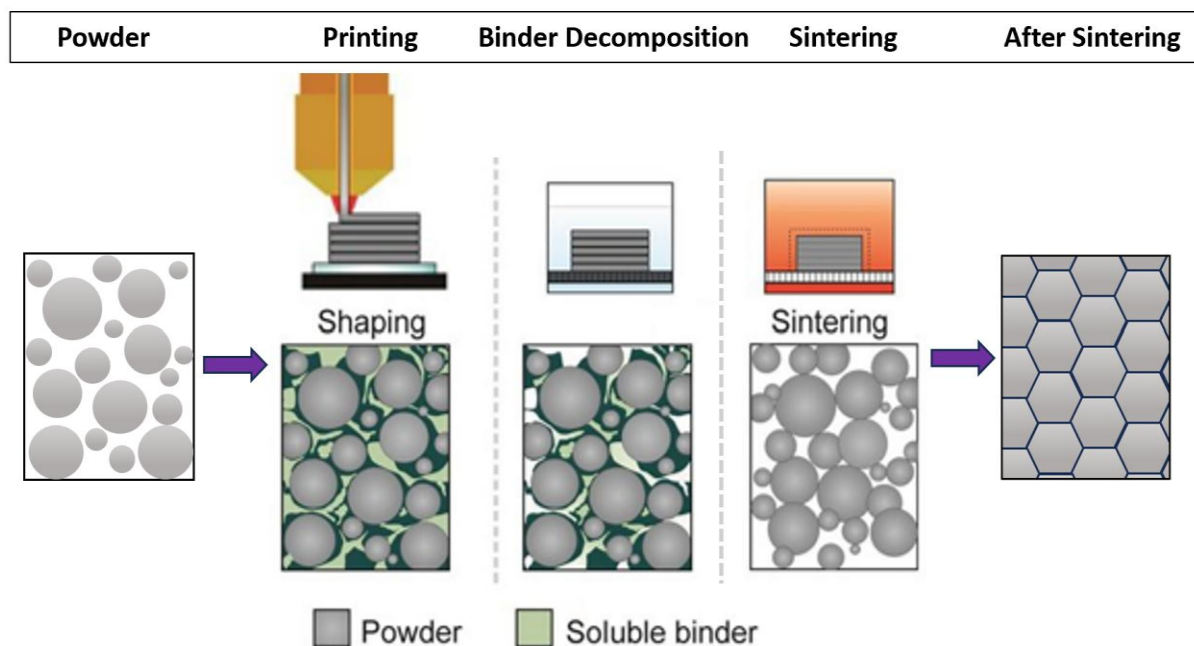


Fig. 2.7: Schematic representation of the Metal Extrusion-based Additive Manufacturing (MEAM) process highlighting the key stages: starting powder feedstock, printing/shaping using a binder-rich filament or paste, binder decomposition (debinding), sintering, and the final densified microstructure after sintering. The illustration shows the transition from loosely packed powder and soluble binder to a fully consolidated structure achieved through thermal processing [57].

2.3.2 Mechanism of Different MEAM Processes

Fig. 2.8 illustrates three widely used extrusion-based additive manufacturing (MEAM) techniques employed for fabricating metal components using polymer-binder or metal-paste feedstock systems [58,59]:

1. Filament-Based Extrusion: This method utilises filaments composed of metal powders mixed with a thermoplastic binder. The filament is fed into a heated nozzle, melted, and extruded layer by layer. It is compatible with conventional fused filament fabrication (FFF) setups, making it an accessible option. However, challenges such as difficulty in achieving high powder loading, filament brittleness, and nozzle clogging limit its effectiveness. These limitations often result in lower green part density and suboptimal sintered properties.

2. Screw-Based Extrusion: This technique uses a hopper-fed screw mechanism to feed paste or pelletized material into a heated nozzle. The continuous operation and consistent material mixing are advantageous, especially for viscous or heterogeneous feedstocks. However, drawbacks include system complexity, higher maintenance requirements, and the risk of binder degradation due to elevated shear and temperature. Issues such as particle segregation and uneven extrusion can also arise.

3. Plunger-Based Extrusion (Paste-Based MEAM): In this approach, a high-solids-loading metallic paste is extruded through a heated nozzle using a motor-driven plunger. It allows

greater control over feedstock flow, supports higher powder concentrations, and requires no filament preparation. This method is cost-effective, highly adaptable, and particularly well-suited for research and prototyping due to its simplicity and ability to tailor binder-powder compositions.

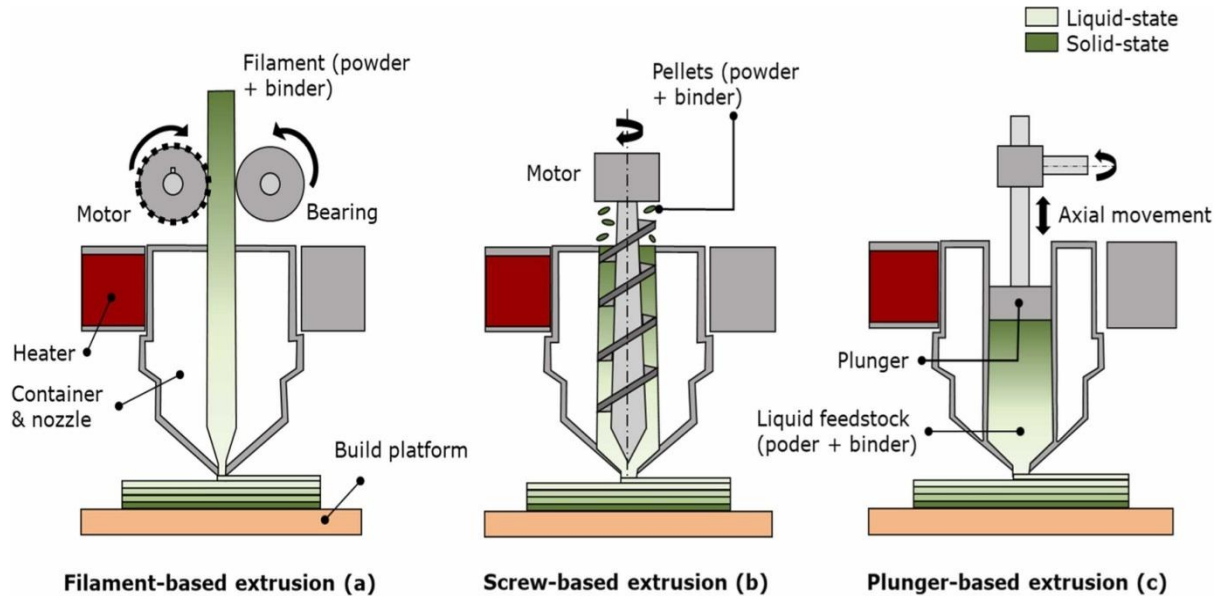


Fig. 2.8: Schematic classification of extrusion-based additive manufacturing (MEAM) processes based on the type of extrusion mechanism employed, (a) filament-based extrusion, (b) screw-based extrusion where a rotating screw conveys paste pelletized feedstock through a heated nozzle, and (c) plunger- or syringe-based extrusion [59]

While all three methods fall under the broader category of material extrusion AM, paste-based extrusion (plunger-driven MEAM) stands out due to its higher powder loading capacity, ease of material handling, and potential for producing near-net-shape parts [58].

Additionally, the deposition or scan strategy plays a pivotal role in determining the structural integrity, dimensional accuracy, and defect evolution in printed components. Unlike fusion-based additive manufacturing, MEAM relies on the controlled extrusion of a metal-loaded paste, where the path followed by the nozzle directly influences the drying behaviour, inter-track bonding, and the accumulation of mechanical stresses.

Different deposition strategies such as linear rastering, concentric circular paths, or complex infill patterns like gyroids, introduce varying mechanical and geometric complexities during extrusion. These strategies can lead to non-uniform drying, local variations in paste distribution, and differential shrinkage during drying and sintering, which are critical factors affecting the final part density and microstructure [60,61].

Importantly, the motion of the extrusion nozzle, governed by stepper motors and mechanical drive systems, is subject to acceleration, deceleration, and frequent directional changes during deposition. These mechanical transitions often lead to start-stop artefacts, including local over-extrusion or under-extrusion, paste smearing, or layer misalignment. Such artefacts arise due to the inertia of the system and the lag in paste response during sudden changes in nozzle velocity or direction. These mechanical-induced defects may manifest as voids, layer shifting, filament overlap, or irregular cross-sectional geometries, especially at corners, junctions, or path inflexion points. As a result, careful optimisation of the scan strategy and motion control parameters is essential in MEAM to ensure uniform layer deposition, effective drying, and defect minimisation, thereby improving the geometric fidelity and mechanical performance of the printed parts [62].

For example, Hosseinimehr et al. [62] systematically studied the influence of different deposition strategies, namely linear, circular, and linear with +10% overfill on the print quality and mechanical performance of stainless steel 316 (SS316) components fabricated using MEAM. Their findings revealed that the linear scan strategy yielded the most uniform material deposition with minimal defect formation, making it the most effective among the tested patterns. In contrast, the circular deposition strategy introduced significant challenges in material flow, resulting in a higher occurrence of internal cavities and voids. This was attributed to the non-uniform paste extrusion during curved nozzle movement, which led to intermittent under-extrusion and inconsistent layer bonding.

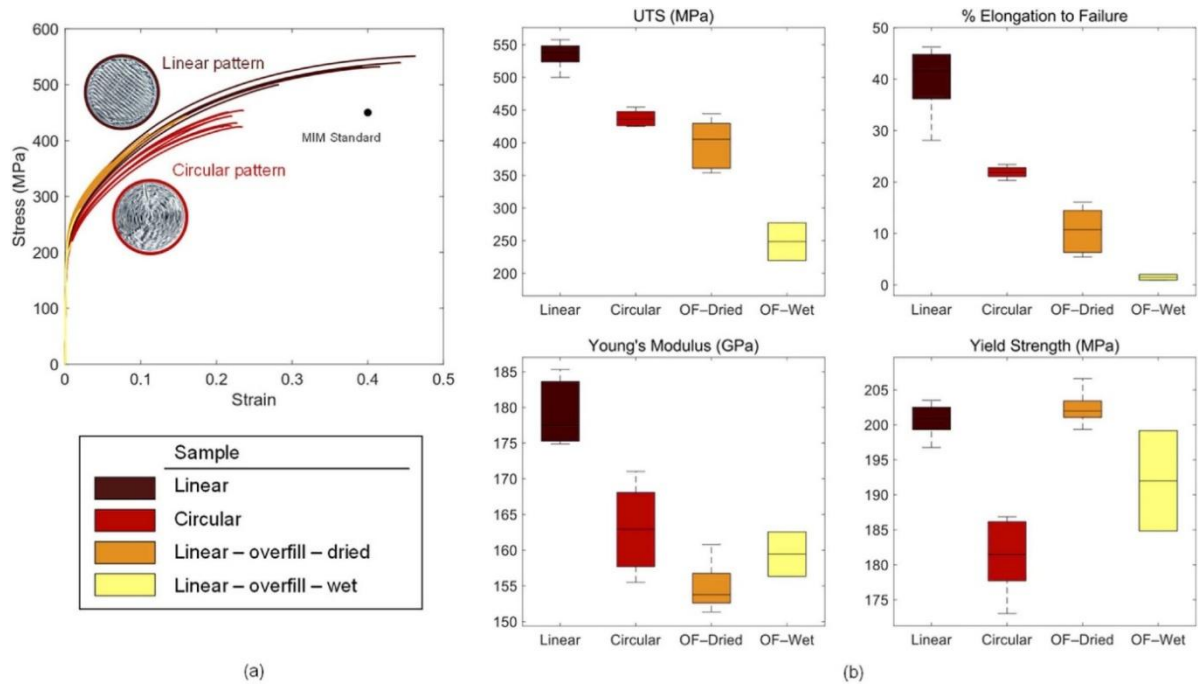


Fig. 2.9: Stress-strain curves of different infill strategies, and (b) Summary of the mechanical properties visualised in various infill strategies [62]

Additionally, the study showed that the linear scan path with a 10% overfill resulted in excessive material accumulation, negatively impacting the dimensional accuracy and surface finish of the printed components. From a mechanical perspective, samples printed with the linear strategy demonstrated superior strength and ductility compared to those produced with circular infill patterns. Fractographic analysis of the circularly printed samples revealed a high density of pores and voids, further confirming the poor extrusion consistency in this pattern. The mechanical properties of various infill strategies are illustrated in Fig. 2.9 (a & b).

Additionally, Go et al. [63] investigated the influence of two distinct scan strategies, namely $0^\circ/90^\circ$ and $-45^\circ/45^\circ$ raster angles, on pore formation in MEAM-fabricated 17-4 PH stainless steel. Their study revealed that the $0^\circ/90^\circ$ raster pattern resulted in relatively larger interlayer pores compared to the $-45^\circ/45^\circ$ configuration after sintering, which negatively impacted the mechanical properties of the sintered parts. The optical images of both the raster patterns are depicted in Fig. 2.10.

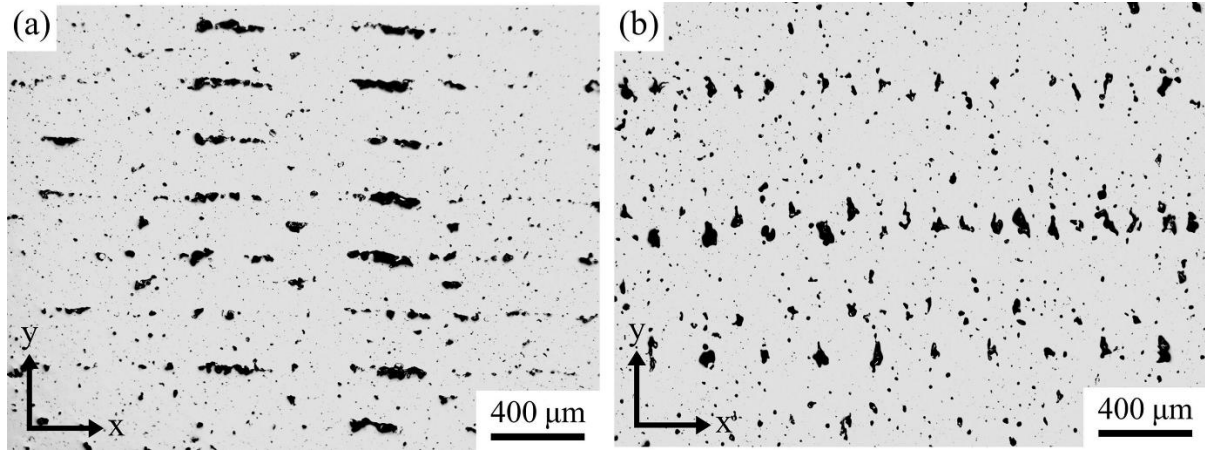


Fig. 2.10: (a & b) optical micrographs of the sintered samples fabricated using the $0^\circ/90^\circ$ and $-45^\circ/45^\circ$ raster patterns, respectively [63].

These findings underscore the critical role of deposition or scan strategy in MEAM, not only in controlling print quality but also in determining the final mechanical performance of the sintered metal components.

2.3.3 Debinding and Sintering Mechanism

2.3.3.1 Debinding

In metal AM processes that utilise binder-based feedstocks, such as MEAM. The removal of the polymeric binder system, commonly referred to as debinding, is a critical step preceding sintering. The purpose of debinding is to eliminate the organic components used to provide shape and strength to the printed green part, without compromising the geometric fidelity or mechanical integrity of the component. The debinding process typically proceeds via thermal debinding, though in some cases, a two-stage debinding approach is adopted, incorporating both solvent and thermal removal mechanisms depending on the binder formulation [64,65]. But in our work, we have only utilised the thermal debinding step to ease the processing, and the paste design is done accordingly.

1. Solvent Debinding

In certain binder systems, particularly those involving multi-component formulations, an initial solvent debinding step is often employed to partially remove the binder before thermal treatment. This process typically involves immersing the green part in an organic solvent which selectively dissolves the soluble binder phase, commonly consisting of waxes or plasticisers. The primary advantage of this approach is that solvent debinding initiates the formation of an interconnected pore network within the part. This pore structure facilitates more efficient gas-phase transport of residual binder vapours during the subsequent thermal debinding stage, reducing the risk of internal defects such as bloating, cracking, or delamination [58,64].

Instead, MEAM processes used in this study typically adopted fully thermally decomposable binder systems. These systems are more environmentally friendly and process-compatible, as they eliminate the need for solvent handling and disposal.

2. Thermal Debinding

Thermal debinding involves the gradual decomposition and volatilisation of the polymeric binder system under controlled heating conditions. This process is typically conducted in an inert (e.g., argon or nitrogen) or reducing (e.g., hydrogen) atmosphere to avoid oxidation of the metal powders. The temperature range for thermal debinding usually lies between 200°C and 600°C, varying according to the type and composition of the binder system. During the thermal debinding cycle, the binder first softens or melts, followed by chemical decomposition into gaseous by-products. These gases diffuse out of the part through capillary channels formed between metal particles. A carefully controlled heating rate is essential to prevent pressure build-up, which can otherwise lead to defects such as bloating, internal cracking, or even collapse of the green body [64]. The schematic representation of thermal debinding is illustrated in Fig. 2.11.

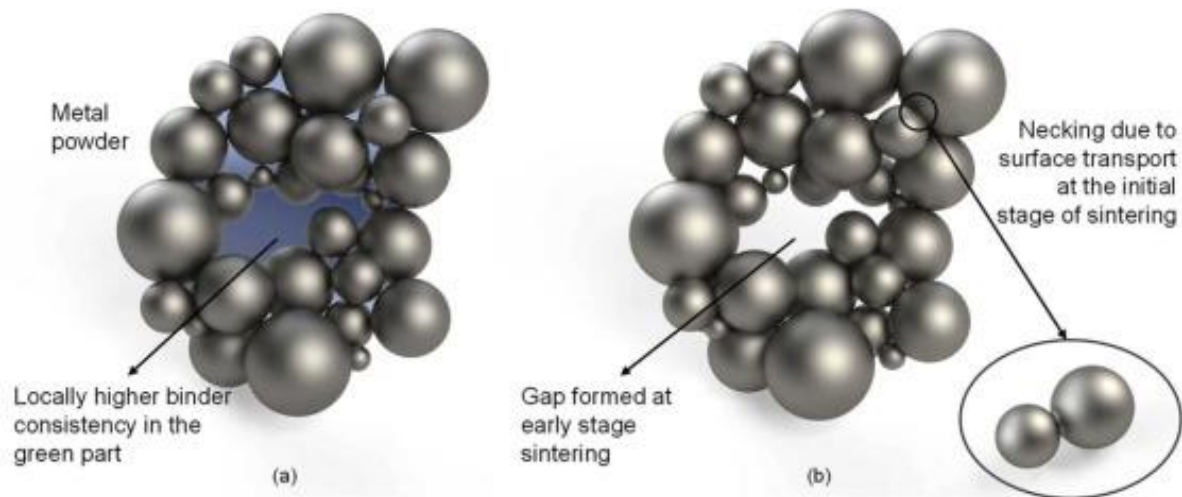


Fig. 2.11: (a) Schematic representation of the internal structure of a green part composed of metal powders uniformly dispersed within a polymeric binder matrix, and (b) Structure of the part after thermal debinding, showing the removal of polymeric binders through thermal decomposition, leaving behind a porous framework of metal powder particles [62].

In one study, Singh et al. [65] used a metal screw-based extrusion process for fabricating components from 17-4 PH stainless steel feedstock. The binder system primarily consisted of PEG, a water-soluble polymer, which enabled the implementation of a hybrid debinding strategy involving both solvent and thermal debinding steps. Initially, solvent debinding was performed by immersing the green parts in water, leveraging PEG's solubility, followed by thermal debinding to remove any residual binders. To optimise the solvent debinding step, they conducted a systematic study of mass loss over time and temperature, testing immersion durations from 0 to 12 hours in water at room temperature and at an elevated temperature of 60 °C, with measurements taken at 2-hour intervals after 4 hours of debinding. As shown in Fig. 2.12, a significantly higher mass loss was observed at 60 °C for 12 hours, which was attributed to enhanced solubility of PEG at elevated temperatures. Based on this observation, 60 °C for 12 hours was selected as the optimal condition for solvent debinding in their process.

Subsequent thermal debinding and high-temperature sintering led to a final relative density of ~96.5%, indicating effective binder removal and good densification.

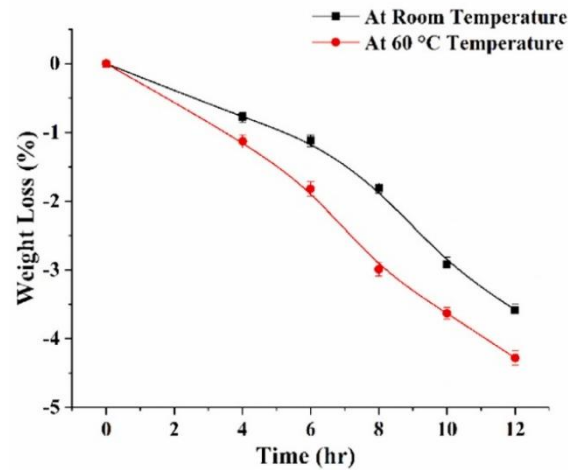


Fig. 2.12: Mass loss recorded during solvent debinding of green part at RT and elevated temperature for different time intervals [65].

In another study, Hosseinimehr et al. [62] employed a metal paste-based extrusion process for the fabrication of components using 316 stainless steel (SS316). Unlike hybrid debinding approaches, their methodology relied solely on thermal debinding, eliminating the need for solvent-based binder removal. This simplified the processing workflow and aligned well with the thermal decomposition profiles of the binders used in their paste formulation. To promote densification and achieve high structural integrity, the authors implemented a high-temperature sintering step following thermal debinding. Through careful optimisation of the sintering parameters, they successfully attained a relative density of ~99.76%, indicating near-full densification of the printed components.

This result demonstrates that paste-based MEAM, even in the absence of solvent debinding, can yield high-density components that closely approach the quality of conventionally manufactured parts, provided that appropriate sintering strategies are applied. In contrast, the inclusion of a solvent debinding step, as seen in the previous study, necessitates the careful

optimisation of time and temperature parameters, thereby increasing processing complexity and duration. By comparing both approaches, it can be concluded that sintering plays a more dominant role in achieving densification, while the debinding steps are primarily critical for binder removal and ensuring the production of contamination-free metal components. Nonetheless, proper optimisation of the debinding process remains essential to prevent defects such as carbon contamination or residual porosity in the final part.

2.3.3.2 Mechanism of Sintering and Densification

Sintering is a crucial step in the MEAM process, as the sintering behaviour and kinetics play a vital role in determining the microstructure and mechanical properties of the final part. The sintering of a material is influenced by several factors such as peak temperature, holding time, heating and cooling rates, and atmosphere, particle size distribution, as all of these directly influence the phase transformations, grain growth, and densification mechanisms. Sintering is a thermally activated process that promotes densification of powder compacts through atomic diffusion. As the green body is heated, metallic particles begin to bond at their points of contact, initiating the formation of sintering necks. These necks gradually grow, while the interconnected pores between particles shrink, become more spherical, and in many cases, close entirely [66]. This evolution in microstructure ultimately yields a dense, cohesive component with enhanced mechanical strength and structural integrity, as illustrated in Fig. 2.13.

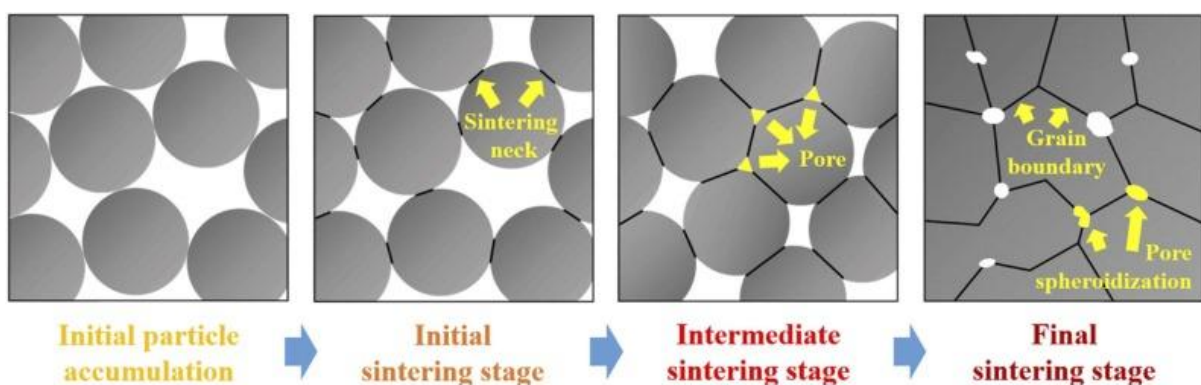


Fig. 2.13: Schematic representation of the sintering process illustrating the evolution of particle bonding and pore structure. As temperature increases, sintering necks form between particles, and pores shrink or close entirely, leading to a denser microstructure with improved mechanical properties [67].

The size, morphology, and distribution of the remaining pores, along with the extent of neck growth, are key indicators of sintering effectiveness. Temperature and dwell time are critical parameters governing the diffusion-driven densification [66]. While higher temperatures facilitate more rapid diffusion and promote densification, excessively high temperatures, particularly those exceeding the melting point, can lead to grain coarsening, distortion, or even melting-induced defects. Therefore, optimising sintering conditions is essential to ensure uniform densification without compromising the dimensional accuracy or structural soundness of the final part [50,68].

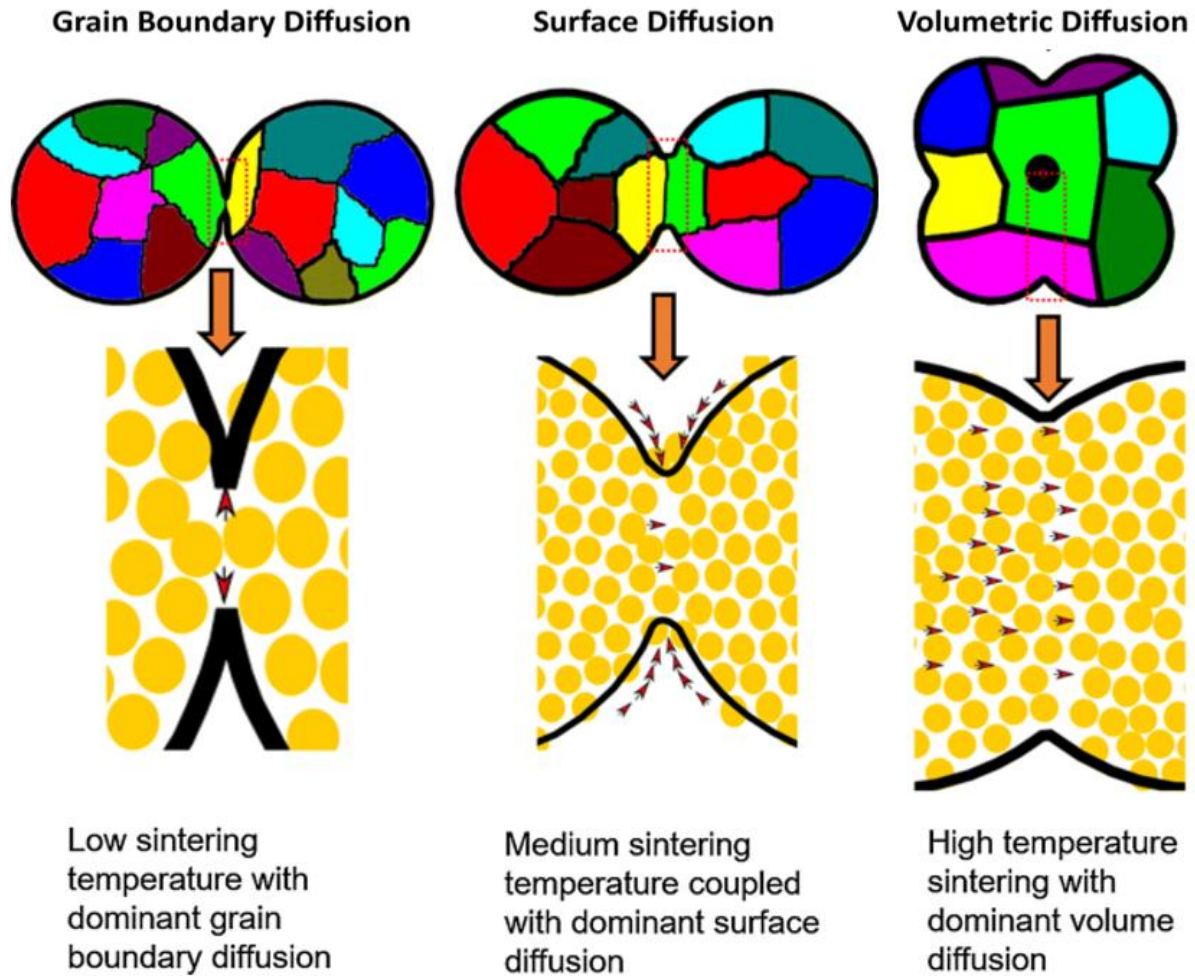


Fig. 2.14: Schematic illustration of the primary diffusion mechanisms involved in the sintering process [69]

The different stages of atomic diffusion during sintering play a crucial role in the densification of the samples. Typically, there are three types of diffusion (grain boundary, surface, and volumetric diffusion). When the material is exposed to lower temperatures during sintering, there is grain boundary (GB) diffusion, where the two particles come in contact, and there is some diffusion of atoms at the contact point. As the temperature rises, surface diffusion plays a dominant role in the transfer of atoms by forming a neck between the two particles and allowing for a greater amount of atomic diffusion. Ultimately, volumetric diffusion dominates when the sintering temperature approaches near the material's melting point. At this point, the necking begins to disappear, the two particles that have been attached by necking become one

particle, and there is a significant volumetric atom diffusion; for this reason, volumetric diffusion plays a crucial role in the final densification of the samples [69]. The mechanism of different diffusion types is illustrated in Fig. 2.14.

Metal Extrusion Additive Manufacturing (MEAM) has demonstrated considerable progress across a wide range of alloy systems, including stainless steels (SS316 and 17-4 PH), titanium alloys (Ti-6Al-4V), and nickel-based superalloys (Inconel 625 and Inconel 718). These materials have shown a promising strength-ductility trade-off, with mechanical properties approaching to those of conventionally manufactured components.

For example, Hosseinimehr et al. [70] used linear strategy in printing and reported a notable decrease in porosity, from 1.12% in the green parts to 0.24% post-sintering, highlighting the effectiveness of the sintering process in enhancing densification. The sintering process effectively reduced the spherical porosities present in the green state. However, it was unable to fully eliminate the elongated voids typically formed due to a lack of proper registry between deposited layers. These inter-layer voids, often aligned along the deposition direction, are indicative of suboptimal layer bonding during the extrusion stage. The uneven pore closure activity of elongated pores is depicted in Fig. 2.15. Impressively, the mechanical properties of the sintered specimens were found to be comparable to those produced via fusion-based AM methods, indicating the capability of MEAM to deliver structurally robust components. Additionally, manganese oxides were detected on the fracture surfaces of the sintered parts. This oxidation was attributed to exposure to non-inert atmospheric conditions during the sintering stage, emphasising the need for controlled and better sintering environments to prevent oxide formation and ensure optimal mechanical performance.

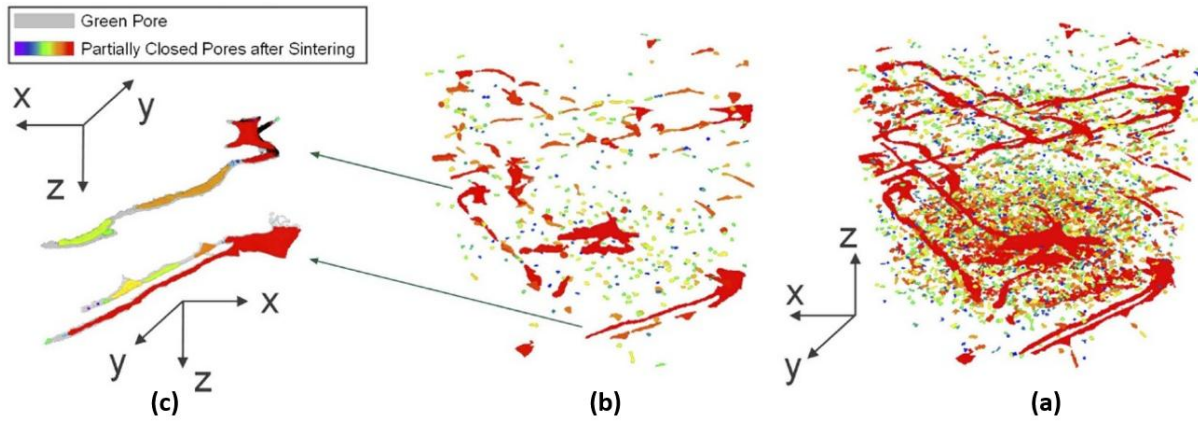


Fig. 2.15: (a) 3D-micro-CT of green part, (d) 3D-micro-CT of sintered part, and (c) 3D visualisation of two large pores originating from the green part, showing partial closure after sintering [70].

Similarly, Singh et al. [65] investigated the effect of sintering temperature on the densification behaviour of 17-4 PH stainless steel fabricated using extrusion-based additive manufacturing. Their study demonstrated that increasing the sintering temperature from 1100 °C to 1360 °C resulted in enhanced densification and improved hardness, primarily attributed to more effective pore closure at elevated temperatures. However, they also observed a progressive coarsening of grains with increasing temperature, which is a common phenomenon during high-temperature sintering due to accelerated atomic diffusion. The optical micrographs corresponding to sintering at 1100 °C, 1200 °C, 1300 °C, and 1360 °C are presented in Fig. 2.16, illustrating the microstructural evolution across the temperature range.

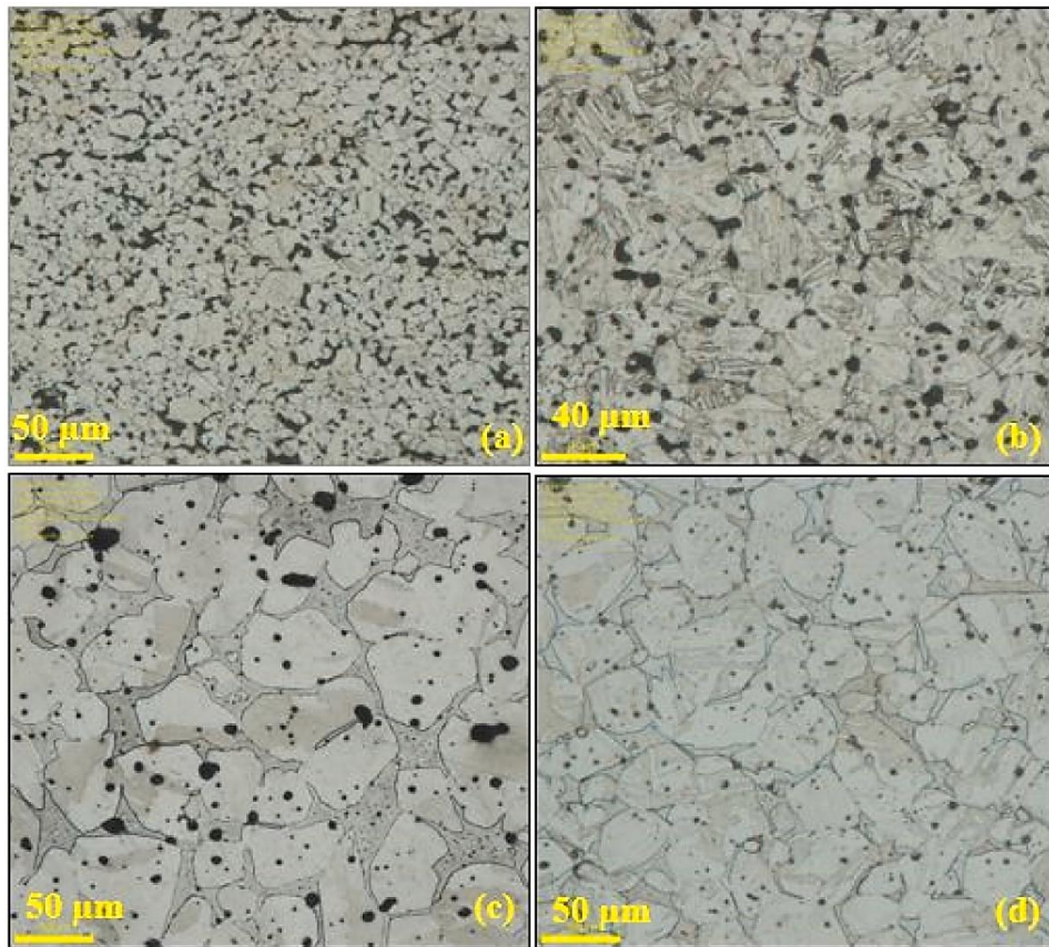


Fig. 2.16: Optical micrographs showing the microstructural evolution of 17-4 PH stainless steel samples sintered at varying temperatures: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, and (d) 1360 °C [65].

Additionally, Go et al. [63] examined the effect of sintering temperature on densification behaviour by conducting sintering at 1230 °C, 1280 °C, 1330 °C, and 1380 °C. The results indicated that increasing the sintering temperature led to improved densification, attributed to enhanced pore closure activity and more effective material diffusion during the sintering process.

In the case of Ni-based alloys, Carrozza et al. [71] investigated the microstructural and mechanical properties of Inconel 625 fabricated using Metal Extrusion-based Additive Manufacturing (MEAM) and reported inferior hardness values compared to those produced via

fusion-based AM techniques. This reduction in hardness was primarily attributed to the presence of significant interconnected elongated porosity. Furthermore, the formation of Nb-, Mo-, and Si-rich carbides was observed within the microstructure. Despite subjecting the parts to an extended high-temperature sintering process lasting 27 hours, a residual porosity of approximately 3% persisted. It is noteworthy that the specific sintering temperature was not disclosed. As illustrated in Fig. 2.17, the elongated and interconnected pores were linked to suboptimal printing and sintering parameters. In addition to mechanical limitations, MEAM-processed Inconel 625 samples exhibited a comparatively higher corrosion rate than those produced by Laser Directed Energy Deposition (L-DED) and Laser Powder Bed Fusion (L-PBF). This increased corrosion susceptibility was associated with grain-dropping phenomena and localised corrosion activity. The study emphasises the critical need for further optimisation of sintering conditions specific to MEAM for Inconel 625, given the limited availability of literature and the challenges in achieving full densification and defect-free parts through current processing protocols.

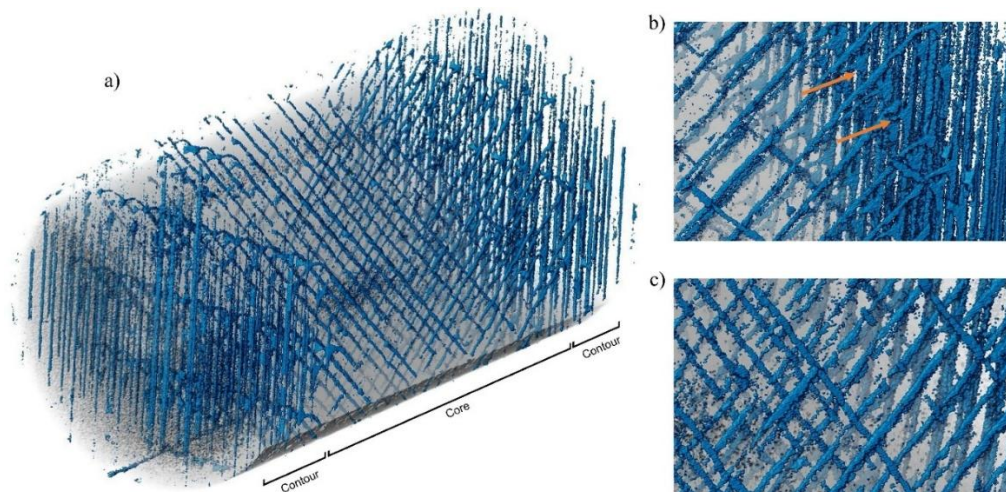


Fig. 2.17: (a) 3D micro-computed tomography (micro-CT) reconstruction of MEAM-fabricated Inconel 625, revealing interconnected elongated porosity, (b and c) macro-level porosity of MEAM-fabricated Inconel 625 components showing prominent grid-like defects [71].

Additionally, Rosnitschek et al. [72] demonstrated that extended thermal debinding and sintering cycles of up to 24 hours could yield favourable strength–ductility trade-offs in MEAM-fabricated components. However, specific sintering temperatures and final porosity values were not reported in their study.

Similarly, Thompson et al. [73] investigated the fabrication of Inconel 718 via metal extrusion additive manufacturing (MEAM) and systematically analysed the effect of sintering temperature on porosity and grain size. Sintering was performed at four distinct temperatures of 1260 °C, 1280 °C, 1300 °C, and 1320 °C, with a constant dwell time of 4 hours. The study revealed a clear trend: increasing sintering temperature led to reduced porosity but also promoted grain coarsening and is illustrated in Fig. 2.18. Among the tested conditions, 1280 °C emerged as the optimal sintering temperature, offering a balance between minimising porosity and restricting excessive grain growth. At temperatures above 1300 °C, significant grain coarsening was evident, potentially detrimental to mechanical performance. Furthermore, across all sintering conditions, the formation of Nb-rich carbides was consistently observed; however, their volume fraction remained below 1%, suggesting minimal carbon uptake during the debinding and sintering processes.

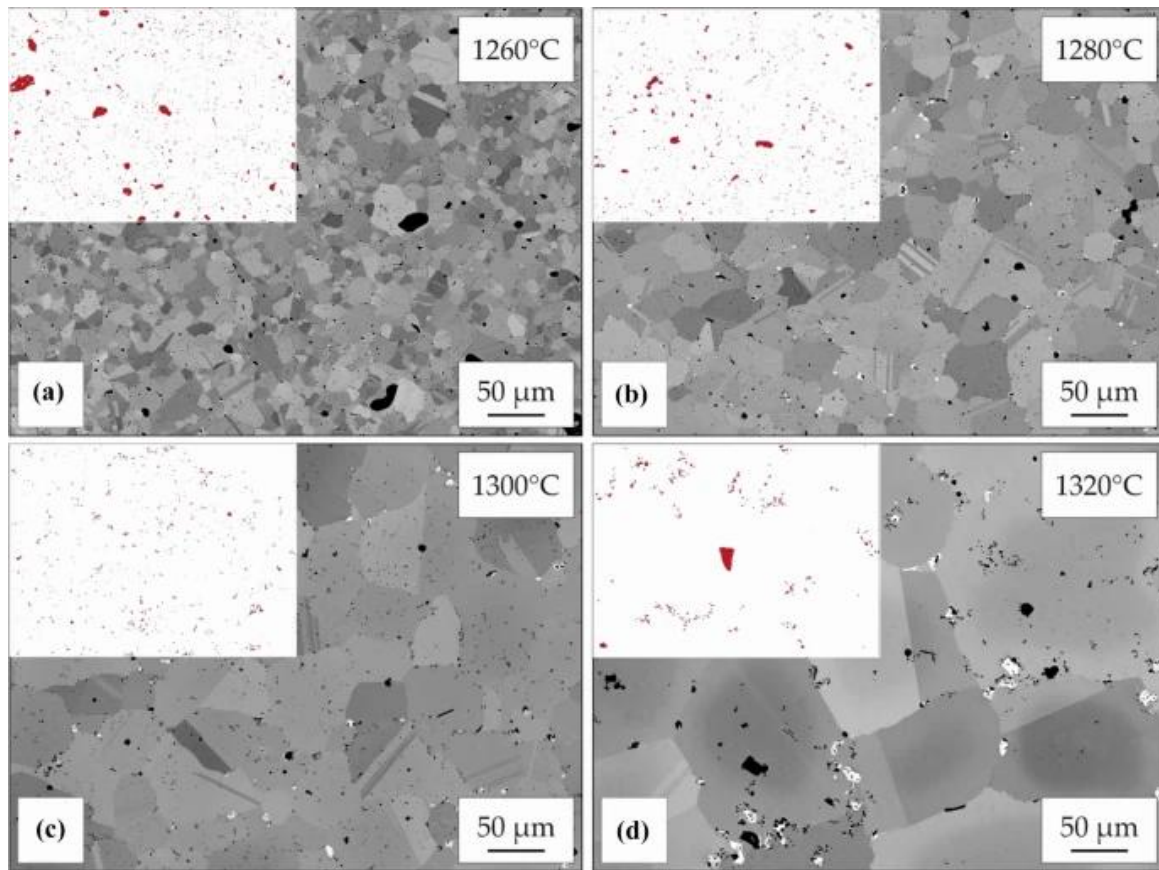


Fig. 2.18: Backscattered electron (BSE) micrographs of Inconel 718 fabricated via MEAM and sintered at different temperatures: (a) 1260 °C, (b) 1280 °C, (c) 1300 °C, and (d) 1320 °C. Insets show binary images highlighting porosity (in red) [73].

Additionally, in the same study, Thompson et al. [73] performed aging heat treatment on MEAM-fabricated Inconel 718 to promote the formation of γ'' and γ' precipitates, which are known to enhance the alloy's mechanical strength. Atom Probe Tomography (APT) analysis, shown in Fig. 2.19, confirmed the presence of both γ'' and γ' precipitates in the aged MEAM Inconel 718 samples. The aging treatment resulted in a significant improvement in tensile strength, reaching approximately 1500 MPa, with an associated elongation of around 6%. While the strength achieved was comparable to that obtained by fusion-based additive manufacturing (AM) processes, the elongation was slightly lower. This reduction in ductility was attributed to the residual porosity present in the MEAM-processed samples.

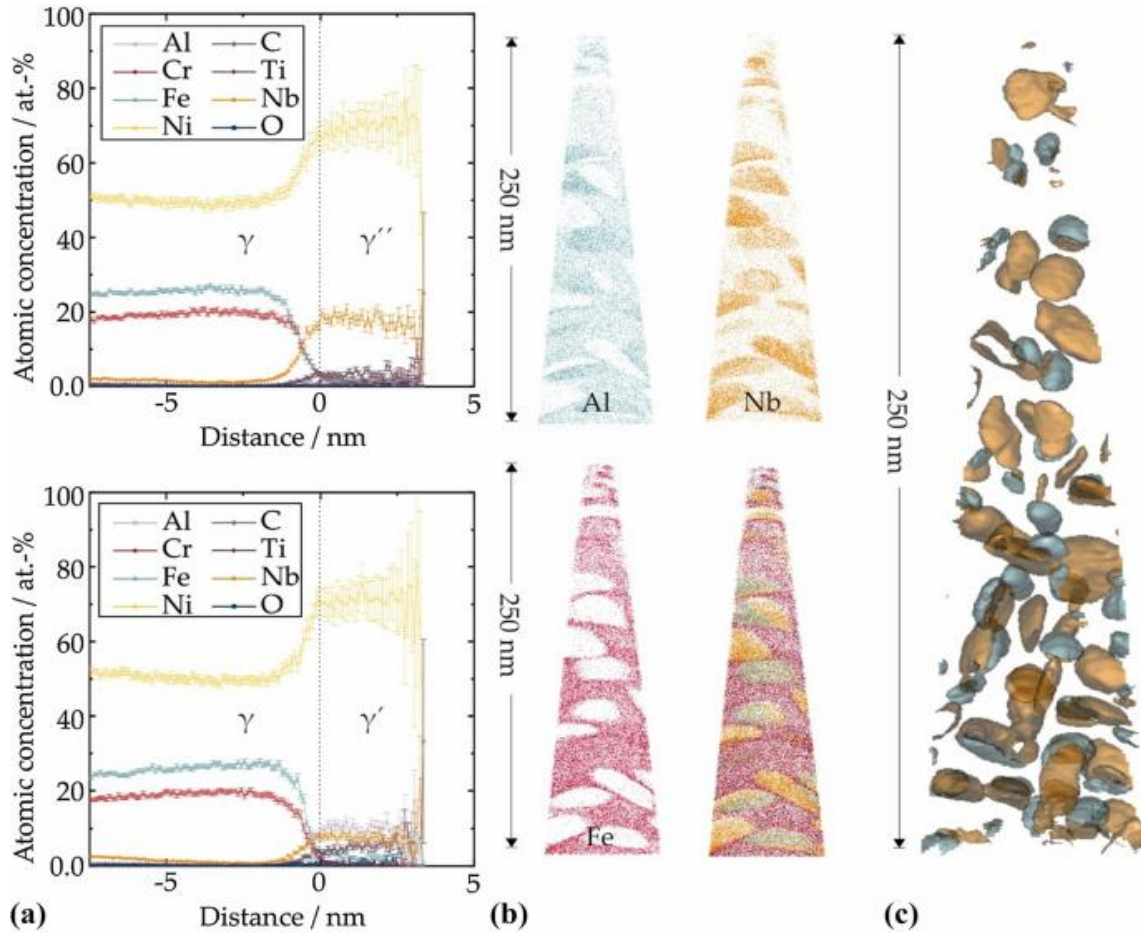


Fig. 2.19: (a) Region of interest (ROI) 1D concentration profiles taken along the matrix and γ'' and γ' precipitates, (b) 3D ion distribution of different solutes, and (c) 3D APT reconstruction using Al and Nb iso-surfaces to represent γ'' and γ' precipitates [73].

Finally, Thomas et al. employed fused deposition modelling (FDM) to fabricate Inconel 625 turbine blade components and reported that non-optimal sintering conditions resulted in significant residual porosity. This finding highlights the critical need for optimisation of sintering parameters to enhance part quality and densification in MEAM-based fabrication of high-performance alloys.

Chapter 3

3. Motivation, Literature Gaps and Objective

3.1 Problem Statement and Motivation

Casting has been a traditional route to fabricating Ni-based superalloys. However, the elemental segregations, shrinkage defects, and the formation of undesirable brittle phases have been a serious concern for industrial applications. The inability to produce complex shapes or intricate geometries has also limited their use in industrial applications. The demand for producing integrated, complex and site-specific components has led to an increased use of AM techniques for the fabrication of Inconel 625. Fusion-based AM methods, such as powder bed fusion and directed energy deposition, have been increasingly utilised to fabricate Ni-based alloys and produce hierarchical microstructures, which yield higher strengths.

Despite its advantages, fusion-based AM of Inconel 625 faces several challenges, including gas porosity, lack of fusion defects, keyhole porosity, vaporisation, and anisotropy. These issues can be mitigated to some extent through careful optimisation of process parameters. However, microcracking remains a significant concern in Inconel 625 and other Ni-based superalloys, and the available literature on the microcracking of Inconel 625 is often inconsistent. To address cracking issues, strategies such as compositional modifications and substrate preheating have been explored. Yet, each approach presents limitations: compositional changes may alter the alloy's inherent properties, while effective preheating often requires high temperatures that exceed the capabilities of most commercially available AM systems. Moreover, although preheating has been shown to reduce microcracking, it has not been entirely successful in eliminating it.

Collectively, these challenges (inherent anisotropy, compositional deviation, and microcracking) limit the ability to consistently produce high-quality, reliable Ni-based superalloy components via fusion-based AM, necessitating further research to overcome these fundamental processing hurdles and unlock the full potential of these advanced materials.

To counter the aforementioned challenges, solid-state AM, such as MEAM, is emerging as a viable solution to counter the solidification-related issues associated with fusion-based AM techniques (e.g., microcracking, anisotropy and loss of alloying elements). MEAM technology has recently gained attention due to its relatively low costs, versatile and eco-friendly process.

3.2. Literature Gaps in MEAM of Inconel 625

Although MEAM is increasingly recognised as a viable alternative to fusion-based AM for high-performance alloys such as Inconel 625, the current literature remains fragmented and lacks systematic insights. In particular, inconsistencies in reporting key sintering parameters, often due to proprietary constraints, have hindered the establishment of process-structure-property correlations. Furthermore, limited studies have directly examined the influence of sintering temperature and duration on densification, porosity evolution, carbide formation, and mechanical performance in MEAM-processed Inconel 625. Therefore, a clear research gap exists in establishing these correlations, which is essential for advancing MEAM toward structural applications demanding high reliability and performance.

3.3 Objective

The objective of this study is to establish how sintering time at high homologous temperatures governs the densification behavior, microstructural evolution, and resulting mechanical performance of Inconel 625 components fabricated via Material Extrusion Additive Manufacturing (MEAM). Rather than only examining processing effects, this work aims to

generate insights into the process–structure–property relationships that define the performance of sintered Ni-based alloys.

Specifically, this research seeks to:

1. Determine the role of sintering duration in influencing porosity evolution, grain structure development, and secondary phase precipitation (carbides and intermetallics) in MEAM-fabricated Inconel 625.
2. Establish correlations between microstructural features and mechanical performance, with emphasis on understanding how differences in porosity fraction and microstructural features contribute to yield strength, ultimate tensile strength and elongation.
3. To compare theoretical yield strength predictions with experimental results in order to evaluate the accuracy and limitations of existing strengthening models.

Chapter 4

4. Materials and Methods

This study uses Inconel 625 powders with micron-scale particle size distributions in combination with a proprietary binder system provided by Rapidia Technologies Inc. The research methodology comprises a systematic set of density measurements and advanced characterisation techniques applied to the sintered components. The morphological and microstructural features of the powders were examined using scanning electron microscopy (SEM). In addition, a comprehensive paste characterisation protocol, including rheological assessments, was conducted to evaluate the processability of the feedstock. Thermal analysis techniques, including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were employed to assess the thermal behaviour of the paste and to design an optimised sintering profile.

Following sintering, the densification of the printed components was quantified using Archimedes' principle and corroborated through micro-computed tomography (micro-CT) to evaluate internal porosity and density distribution. To investigate the phase evolution, X-ray diffraction (XRD) analysis was conducted on samples sintered for both short and extended durations. Further, SEM-based energy-dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) analyses were performed to study the elemental distribution and grain structure evolution, respectively. Finally, tensile testing was carried out on both sets of sintered samples to establish a robust structure–property correlation.

4.1 Materials

4.1.1 Powder

In the present investigation, gas-atomised Inconel 625 powder, procured from Finida, was utilised as the primary feedstock material. The chemical composition of the as-received powder

is provided in Table 4.1. The powder exhibited a near-spherical morphology with an average particle size (d_{50}) of $\sim 6\ \mu\text{m}$, as determined by particle size analysis (Image J software). A representative scanning electron microscopy (SEM) image of the Inconel 625 powder is shown in Fig. 4.1, highlighting its morphological characteristics and surface texture.

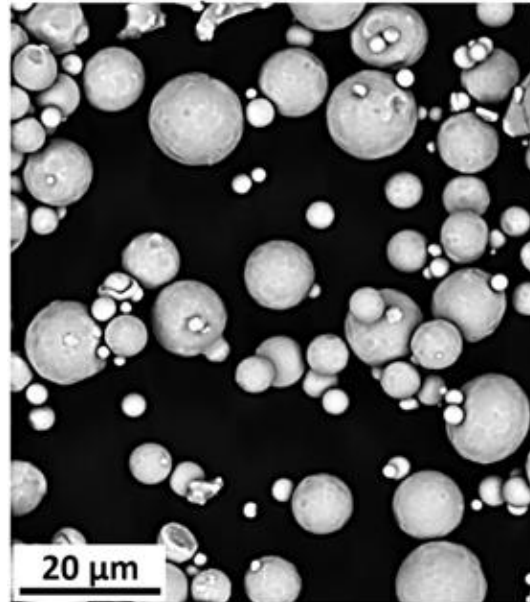


Fig. 4.1: SEM image of as-received Inconel 625 powder

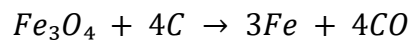
Table. 4.1: Nominal composition of Inconel 625 powder used for the current study in wt% (bal. Ni).

Elements	Ni	Cr	Mo	Nb	Fe	Si	Co	Ti	C
Composition (wt%)	Bal	21.01	8.66	3.73	2.63	0.28	0.12	0.072	0.018

To mitigate residual carbon originating from the binder during sintering, the Inconel 625 powder was modified by blending with 0.3 wt% Fe_3O_4 powder. This blending was carried out using a low-energy ball mixing process, which is fundamentally distinct from high-energy ball milling in terms of its mechanical impact and intended purpose. The ball mixing was performed at a rotational speed of 120 rpm for 30 minutes, with a directional change from clockwise to

anticlockwise after 15 minutes to promote uniform distribution of Fe₃O₄ throughout the Inconel 625 matrix.

The primary objective of this step was to achieve a homogeneous dispersion of Fe₃O₄ particles within the metallic powder without inducing any significant changes in particle size or morphology. During the subsequent sintering process, Fe₃O₄ serves as a carbon scavenger, reacting with residual carbonaceous species derived from the binder decomposition. This redox reaction facilitates the formation of gaseous by-products, thereby reducing the carbon content in the final sintered Inconel 625 components. The overall reduction reaction governing this carbon removal mechanism is expressed as:



This approach is aimed at limiting unwanted carbide formation and enhancing the microstructural integrity of the sintered parts.

4.1.2 Paste

To prepare a suitable feedstock for metal extrusion additive manufacturing (MEAM), a paste was formulated by thoroughly mixing the modified Inconel 625 powder with a carefully selected binder system, dispersing agent, and water. The purpose of this formulation was to ensure optimal rheological properties for extrusion while maintaining the mechanical integrity of the green bodies prior to sintering. The composition of the paste consisted of 1-20 wt% water and 1-10 wt% binder and dispersing agents, which were adjusted to achieve a homogeneous and extrudable consistency. The binder system used in this investigation comprised polyethylene glycol (PEG) and polyvinyl alcohol (PVA). PEG played a crucial role in providing temporary cohesion and flowability of the paste during the extrusion and printing process, ensuring smooth deposition without clogging or discontinuities. Meanwhile, PVA enhanced the mechanical strength and dimensional stability of the green parts, allowing them to be handled, stored, and transferred to the sintering furnace without compromising their structural integrity.

This dual-binder approach was essential in producing defect-free green parts that could withstand post-processing without deformation.

It is important to note that the exact composition of the binder system remains proprietary to Rapidia Tech Inc. and cannot be disclosed. However, it is confirmed that the system includes only PEG, PVA, and water, with no additional plasticisers or additives. The choice of these materials was due to the water solubility, thermal decomposition characteristics, and prior successful implementation in MEAM systems. The SEM image of the paste is presented in Fig. 4.2, showing a relatively uniform and spherical morphology of Inconel 625 particles in the binder, which is favourable for consistent flow behaviour and dense packing in the final printed components.

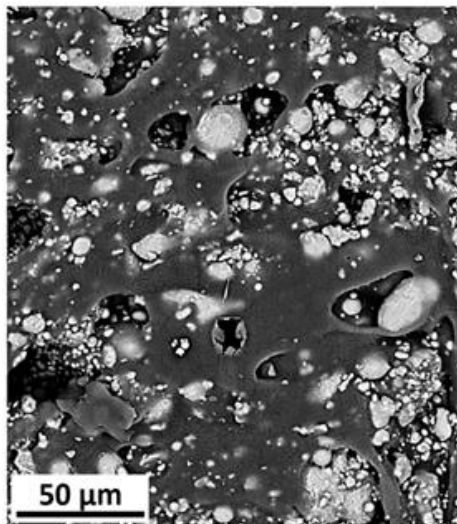


Fig. 4.2: Scanning Electron Microscope (SEM) image of the formulated paste comprising Inconel 625 powder blended with a proprietary binder system.

Additionally, to validate the printability and flow characteristics of the prepared Inconel 625 paste, rheological assessments were carried out using a Discovery HR 20 rheometer. The rheological data, depicted in Fig. 4.3 (a & b), indicate a significant decrease in viscosity with increasing shear rate, a typical signature of non-Newtonian, shear-thinning behaviour. This rheological characteristic is crucial for extrusion-based additive manufacturing, as it ensures

smooth flow under shear (during extrusion) while maintaining structural integrity post-deposition.

The relationship governing the shear stress (τ) of a non-Newtonian fluid is described by the power-law model:

$$\tau = k \frac{du^n}{dy}$$

where du/dy represents the shear rate, and k and n are material-specific constants. For the Inconel 625 paste studied here, the shear rate exponent n was determined to be 0.88 (see Fig. 4.3b), further confirming its shear-thinning nature. Such behaviour is highly desirable for paste extrusion, enabling high shape fidelity and stable layer deposition.

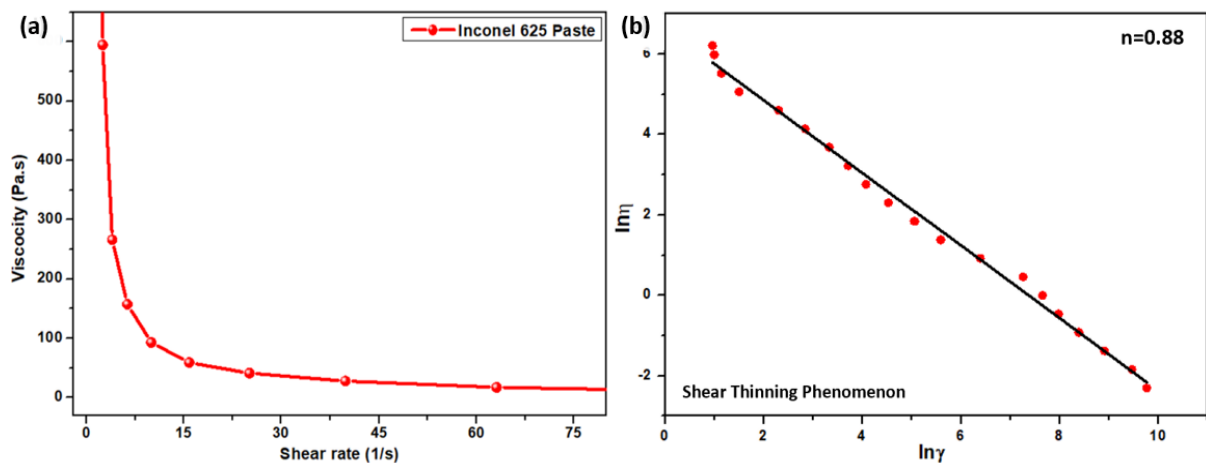


Fig. 4.3: (a) Paste rheology (viscosity vs shear rate), and (b) $\ln(\eta)$ vs $\ln(\gamma)$ depicting the shear thinning phenomenon. Where, η is the viscosity and γ is shear rate.

4.2 Methods

4.2.1 Printing

The prepared Inconel 625 paste was subsequently transferred into a dedicated cartridge, which was then installed into the Rapidia Tech Inc. Conflux 1 metal extrusion additive manufacturing (MEAM) system. In this setup, the extrusion process is governed by a controlled plunger mechanism that applies uniform pressure to the paste within the cartridge, thereby forcing it through the printing nozzle. The deposition head of the Rapidia Conflux 1 MEAM printer,

which governs the precision extrusion and placement of the paste, is illustrated in Fig. 4.4 (a & b). The complete set of printing parameters employed in this study, including layer height, nozzle diameter, extrusion speed, and build platform temperature, is detailed in Table 4.2.

To generate machine-readable instructions for the printing process, the Rapidia Cura slicing software was used to convert 3D CAD models into a series of layer-by-layer toolpaths. Once sliced, the printer executed the deposition sequence by extruding the paste directly onto the substrate in a predetermined pattern. Concurrently, a halogen lamp was systematically scanned after the deposition of each individual layer. This in-situ drying mechanism facilitated the rapid evaporation of water from the binder system, promoting partial solidification and dimensional stability of the green parts before debinding and sintering.

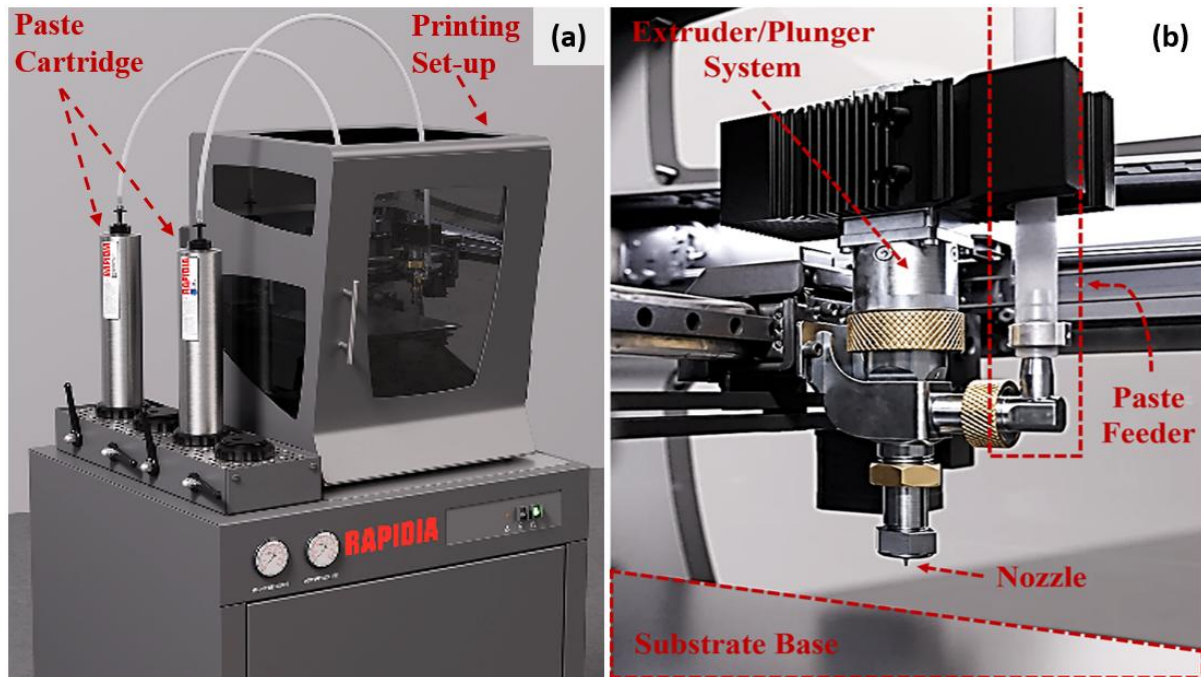


Fig. 4.4: (a) The Rapidia Conflux 1 metal extrusion additive manufacturing (MEAM) system featuring dual paste cartridges connected to the printing chamber, and (b) Close-up view of the deposition head showing the extruder/plunger system, paste feeder, and nozzle arrangement.

Table. 4.2: Parameters used for printing Inconel 625 using Rapidia Tech Inc. Conflux 1 MEAM

Parameters Used	Values
Water pump pressure	689.5 kPa
Nozzle diameter	0.4 mm
Flow rate	10 cc/hr
Printing speed	40 mm/s
Layer thickness	0.25 mm
Printing strategy	Linear strategy
Layer rotation	0° rotation

4.2.2 Sintering Cycle and DSC Analysis

Following extrusion, the green parts were transferred to a Rapidia Tech Inc. F2 furnace with inert and vacuum environment capabilities. The sintering of the printed Inconel 625 components followed a carefully designed multi-stage thermal profile, illustrated in Fig. 4.5(a). This profile consisted of two sequential thermal debinding stages, one at 300 °C and the other at 600 °C, each maintained for 1 hr to ensure the effective removal of binder constituents from the green parts. These stages were followed by a high-temperature sintering step at 1290 °C to promote densification and microstructural consolidation. To evaluate the influence of sintering duration on the densification behaviour, microstructural evolution, and mechanical performance, two distinctly different holding times at the peak sintering temperature were investigated: a short duration of 5 mins and a long duration of 4 hrs. These time intervals were deliberately chosen to provide a pronounced contrast in the extent of sintering, allowing for a comprehensive understanding of how prolonged thermal exposure affects grain growth, porosity elimination, phase transformation, and overall structural uniformity. Additionally, the comparison aims to correlate these microstructural differences with the resulting mechanical properties such as strength, ductility, and fracture characteristics.

The furnace chamber was initially evacuated to a high vacuum level ranging between 1-10 Torr until the temperature reached approximately 200 °C. Following this, ultra-high-purity argon gas (99.995%) was introduced to establish an inert atmosphere suitable for sintering, thus preventing oxidation or contamination during the high-temperature process. After completing the sintering cycle, the components were allowed to cool naturally inside the furnace to room temperature.

To design and simulate this thermal cycle, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted over a temperature range of 20–1320 °C. As shown in Fig. 4.5(b), a significant mass loss was observed up to ~300 °C, corresponding to the first stage of binder decomposition, primarily due to the vaporisation of low molecular weight components in the binder system. The second debinding stage at ~600 °C showed a more gradual mass reduction, indicating the breakdown of more stable polymeric constituents. Above 600 °C, no substantial mass loss was observed, confirming the complete removal of binders. The final sintering stage exhibited thermal stability, with densification occurring without measurable mass reduction. The melting point of the Inconel 625 paste was observed to be around ~1293 °C, and the sintering temperature of 1290 °C was therefore selected to be just below the melting threshold, ensuring optimal densification without risking part distortion.

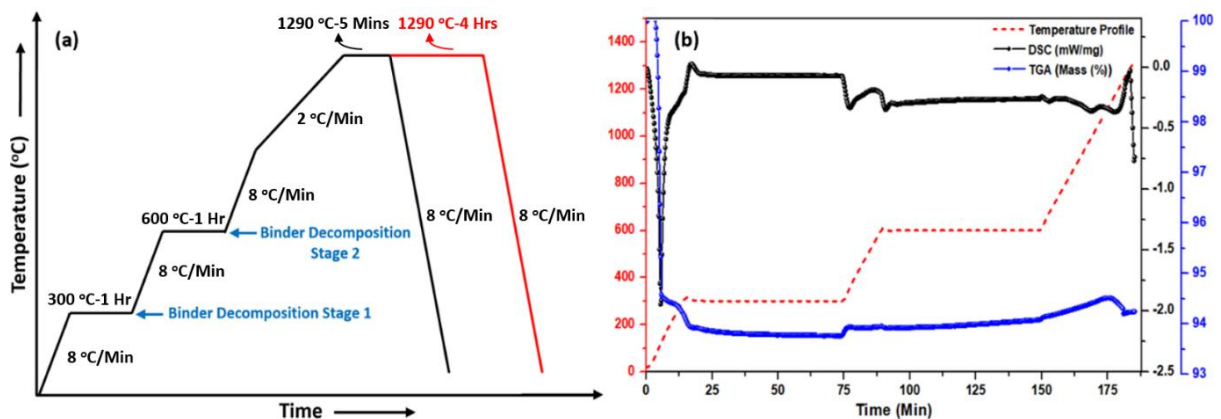


Fig. 4.5: (a) Sintering profile and (b) DSC and TGA of the Inconel 625 paste to simulate the sintering cycle

4.2.3 Archimedes Density

Archimedes density was performed to determine the bulk density of the samples using deionised water as the immersion medium. Three sets of samples were tested for each condition to ensure consistency and reproducibility. The density (ρ) was calculated using the relation:

$$\rho_{bulk} = \frac{m_{air}}{m_{air} - m_{water}} \times \rho_{water}$$

Where m_{air} and m_{water} are the mass of the sample in air and water, respectively. ρ_{water} is the density of water and is assumed to be 0.998 g/cc at room temperature. The relative density of each sample was calculated by comparing the measured bulk density (ρ_{bulk}) to the theoretical density ($\rho_{theoretical}$) of Inconel 625 (8.44 g/cc), using the following equation:

$$Relative\ Density\ (\%) = \left(\frac{\rho_{bulk}}{\rho_{theoretical}} \right) \times 100$$

4.2.4 Micro-Computed Tomography (micro-CT) Analysis

Micro-computed tomography (micro-CT) analysis was performed on the grip ends of the dog bone tensile specimens after tensile testing to evaluate the internal porosity characteristics, including the volume fraction, morphology, and spatial distribution of pores, in the sintered Inconel 625 components. The scans were conducted using a Zeiss Xradia 520 Versa micro-CT system, which provides high-resolution imaging suitable for dense metallic materials. An accelerating voltage of 150 kV was employed to achieve sufficient X-ray penetration through the nickel-based alloy, and the scans were performed at a voxel resolution of 6 μm , enabling the detection of fine-scale internal defects. The acquired CT data were reconstructed into three-dimensional models using Dragonfly Pro software for detailed visualisation and quantitative analysis of the pore structure. The complete set of scanning parameters is summarised in Table 4.3.

To ensure the consistency and statistical reliability of the porosity measurements, two specimens per sintering condition were scanned and analysed. This decision was motivated by the inherent difficulty of achieving sufficient contrast between the dense Ni-based matrix and internal defects, which arises due to the high X-ray attenuation coefficient of Inconel 625. Ni-based alloys are particularly challenging for X-ray CT imaging because the X-rays are significantly absorbed, requiring higher voltages and longer exposure times to generate distinguishable signals from voids and inclusions. Each scan required over 8 hours of continuous operation, making the process time-intensive and costly. As a result, increasing the number of scans to three per condition was not feasible and within the scope of this study.

Table. 4.3: Micro-CT scanning parameters used for Inconel 625

Parameters	Value
X-ray voltage	150 kV
X-ray Current	67 μ A
X-ray power	10.05 W
Voxel Size	6 μ m
Exposure time	17 s

4.2.5 XRD Analysis

X-ray diffraction (XRD) analysis was conducted to identify the phases present in the sintered Inconel 625 samples. A Bruker D8 Discover diffractometer equipped with a VÅNTEC-500 two-dimensional (2D) area detector was employed for this purpose. The measurements were carried out using a Cu-K α radiation source with a wavelength of $\lambda = 1.5418$ Å, operated at an accelerating voltage of 40 kV and a tube current of 40 mA to ensure adequate beam intensity and resolution.

The scan was performed over a 2θ range from 30° to 100° , using a step size of 0.02° , which allowed for high-resolution phase detection and accurate peak identification. The wide scan

range was selected to capture all relevant diffraction peaks associated with the γ -matrix of Inconel 625 and potential secondary phases, such as carbides or Laves phases, which may form during sintering. The 2D area detector enhanced the data acquisition speed and allowed for efficient collection of diffracted intensities with improved signal-to-noise ratios.

4.2.6 SEM, EDS and EBSD Analysis

To investigate the microstructural evolution of the sintered Inconel 625 components, small cylindrical specimens were sectioned from the grip ends of the tensile bars. These regions were chosen to avoid any deformation introduced during mechanical testing. The samples were prepared for microstructural analysis using standard metallographic techniques. Initial preparation involved sequential grinding with SiC abrasive papers, followed by fine polishing using diamond suspensions to achieve a near-mirror finish.

For the final surface preparation prior to electron backscatter diffraction (EBSD), vibratory polishing was carried out using a VibroMet 2 Vibratory Polisher. A colloidal silica suspension (OPS – Oxide Polishing Suspension) was employed as the polishing medium to achieve a high-quality, deformation-free surface suitable for EBSD analysis. This final polishing step was critical for improving the quality and indexing rate of EBSD maps by removing any residual surface deformation from mechanical polishing.

Microstructural characterisation was conducted using a Tescan Vega 3 scanning electron microscope (SEM). The SEM was equipped with a Bruker XFlash 6-10 energy-dispersive X-ray spectroscopy (EDS) detector for elemental analysis and a Bruker eFlashFS electron backscattered diffraction (EBSD) detector for crystallographic orientation mapping. All imaging and analytical data were acquired at an accelerating voltage of 20 kV to ensure optimal resolution and penetration.

EBSD data were collected using a step size of 1.5 μm , which provided an effective balance between scan resolution and area coverage. The collected EBSD datasets (.ctf files) were processed and analysed using TSL-OIM software, which allowed for the generation of inverse pole figure (IPF) maps, grain boundary character distributions, and texture analysis. The integration of EDS and EBSD analyses provided a comprehensive understanding of the microstructural characteristics and phase evolution of the Inconel 625 samples subjected to different sintering conditions.

4.2.7 Tensile Testing

Horizontal cylindrical rods of Inconel 625 were printed with initial dimensions of 14 mm in diameter and 150 mm in length. These printed rods were subsequently machined into standard tensile specimens following the ASTM E8 guidelines. The final geometry of the tensile samples featured a gauge length of 25 mm, a gauge diameter of 6 mm, a jaw length of 40 mm, a total width of 8 mm, and an overall specimen length of 109 mm. A schematic of the machined tensile specimen dimensions is illustrated in Fig. 4.6. Tensile testing was performed using a universal testing machine under a constant strain rate of 10^{-3} s^{-1} , which ensured a uniform and controlled deformation regime, enabling accurate measurement of mechanical properties such as yield strength, ultimate tensile strength, and elongation. A minimum of three specimens per sintering condition were tested to validate the repeatability and statistical consistency of the obtained results.

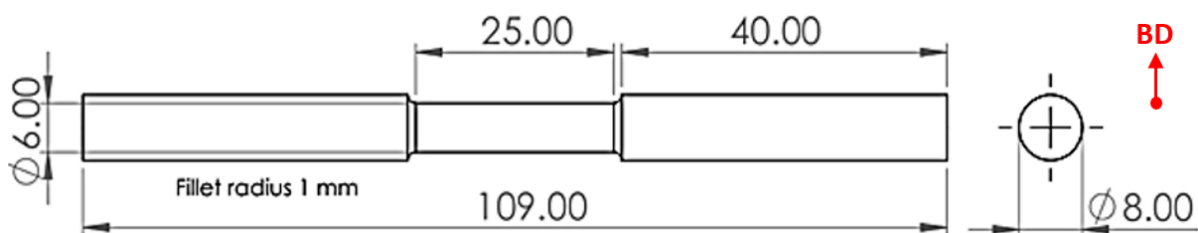


Fig. 4.6: Dimensions of the tensile specimens used in this study (All dimensions are in mm).

Chapter 5

5. Results

5.1 Densification Analysis

The final stage of sintering was performed at 1290 °C to increase the rate of diffusion and reduce the time for densification of the printed samples. Archimedes density measurements showed that the 5 mins sintered sample had a relative density of 98.25% ($\pm 0.17\%$) with a porosity fraction of 1.75% ($\pm 0.17\%$), while the 4 hrs sintered sample exhibited a higher relative density of 99.44% ($\pm 0.20\%$) and a correspondingly lower porosity of 0.56% ($\pm 0.20\%$), indicating that longer sintering significantly improved densification and reduced porosity. Similarly, Fig. 5.1 (a & b) shows the micro-CT analysis of the 5 mins and 4 hrs sintered samples.

The 5 min sintered sample exhibited an overall porosity of $\sim 1.5\%$ - $\sim 1.6\%$. There is elongated interconnected porosity near the periphery of the 5 min sintered sample, which can also be seen in the 2D sliced micro-CT images, from which it can be seen that the inter-track voids are due to the lack of registry in printing. Such voids are difficult to remove in densification [70, 74]. But at longer sintering times, there is a greater chance for such void closure due to the greater amount of volumetric diffusion. Small spherical pores ($< 10\ \mu\text{m}$) were also observed throughout the bulk of the 5 min sintered sample, which is likely due to the initial gas entrapment in the powder or pore entrapment during grain coalescence during sintering. The 4 hrs sintered sample exhibited a lower overall porosity ($\sim 0.5\%$) compared to the 5 mins sample, due to the longer sintering time, which allowed for greater diffusion and pore closure. It can also be seen that the porosity in the 4 hrs sample tends to be dominated by the presence of small spherical pores with minimal elongated pores.

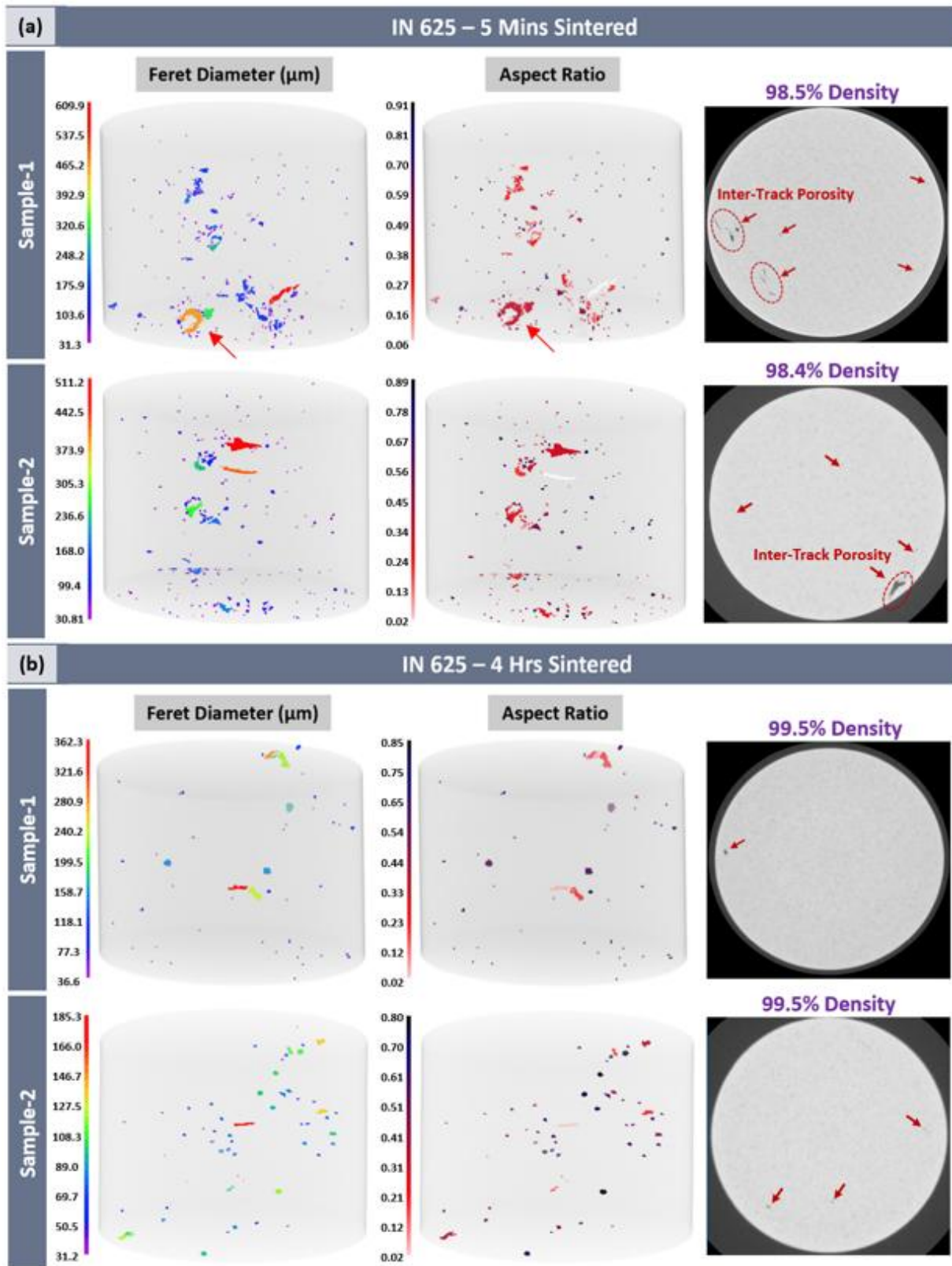


Fig. 5.1: Micro-computed tomography (micro-CT) analysis of sintered samples: (a) 5 mins sintering and (b) 4 hrs sintering. Shown are quantitative measurements of pore morphology,

including mean Feret diameter and aspect ratio, as well as representative 2D X-ray projection images. The data illustrate the evolution of porosity and densification as a function of sintering time.

The quantitative pore analysis is given in Fig. 5.2 (a & b), from which it can be seen that the average mean ferret size (porosity size) is slightly larger in 4 hrs sintered samples (72 μm) when compared to the 5 mins sintered samples (65.5 μm), but the 5 min sintered sample had greater overall porosity. The average pore size in the 4 hrs sintered samples demonstrated strong repeatability (73 μm vs. 71 μm), suggesting uniform densification. For the 5 mins sintered samples, a larger deviation was observed (71 μm vs. 60 μm), likely due to uneven pore closure at shorter sintering durations. Nevertheless, the variation remained within an acceptable tolerance range, considering the short sintering duration and the inherent non-uniformity of early-stage densification. Moreover, it is clear from the histogram in Fig. 5.2 (a & b) that the 4 hrs sintered sample has a slightly higher aspect ratio of ~ 0.51 when compared to the ~ 0.47 of the 5 mins sintered sample, where aspect ratio is given by the ratio of the smallest pore dimension to the largest pore dimension, confirming the pores in the 5 mins sample tend to be more elongated than in the 4 hr sample due to the interconnected inter-track porosity in the former.

The Archimedes density measurement showed a porosity fraction of $\sim 1.75\%$ for the 5 mins sintered sample, while micro-CT analysis indicated a slightly lower porosity of $\sim 1.5\%$. This level of variation in porosity fraction is generally acceptable and can be attributed to pores smaller than the voxel size of the micro-CT scan. In addition, the Archimedes method does not account for closed pores and is therefore less reliable for quantifying porosity compared to micro-CT. On the other hand, both Archimedes and micro-CT methods showed nearly similar porosity fractions for the 4 hrs sintered sample.

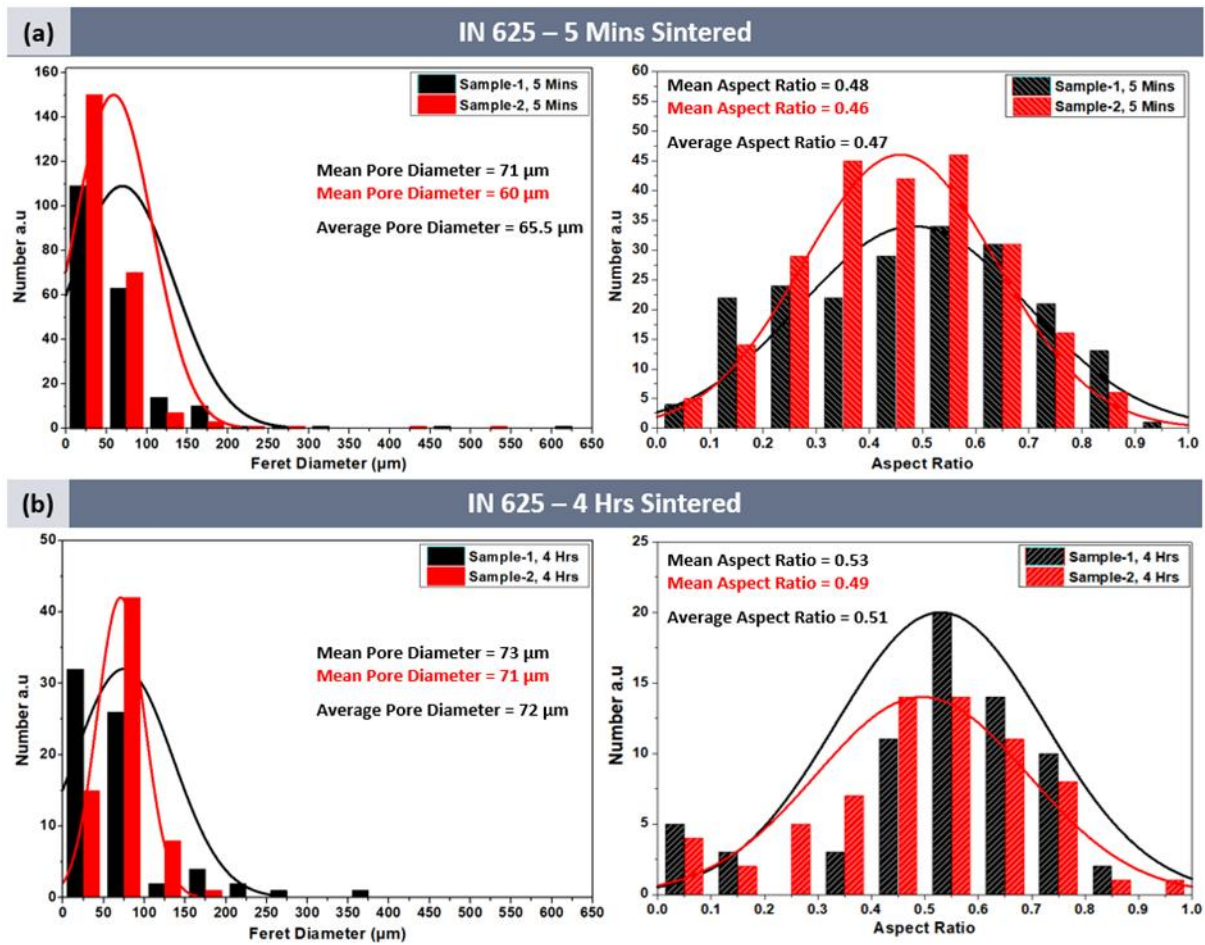


Fig. 5.2: Histogram analysis of pore morphology for sintered Inconel 625 samples: (a) 5 mins sintered samples and (b) 4 hrs sintered samples. In each case, the first plot shows the distribution of pore mean Feret diameter, while the second plot shows the distribution of pore aspect ratio.

5.2 Microstructural Analysis

Fig. 5.3a shows the XRD data of 5 mins and 4 hrs sintered samples. Peaks corresponding to the γ -Ni matrix can be clearly seen. Additionally, comparatively small peaks corresponding to (Nb+Mo)C can also be seen for both samples, which were precipitated during sintering. It was well known that during the solidification of Ni-based alloys, the liquid transforms to γ -Ni matrix and NbC-type interdendritic particles [75,76]. Solid-state precipitation of NbC has been previously observed in Inconel 625 when exposed to temperatures $> 850\text{ }^{\circ}\text{C}$ [77], as the free

energy driving force for the formation of metal carbides (17 KJmol^{-1}) is comparatively higher than for nucleation of the Laves phase (2.9 KJmol^{-1}) at a temperature of 1150°C . The formation of NbC has been noted to increase the room- and high-temperature strength but decrease the ductility of Inconel 625 [77].

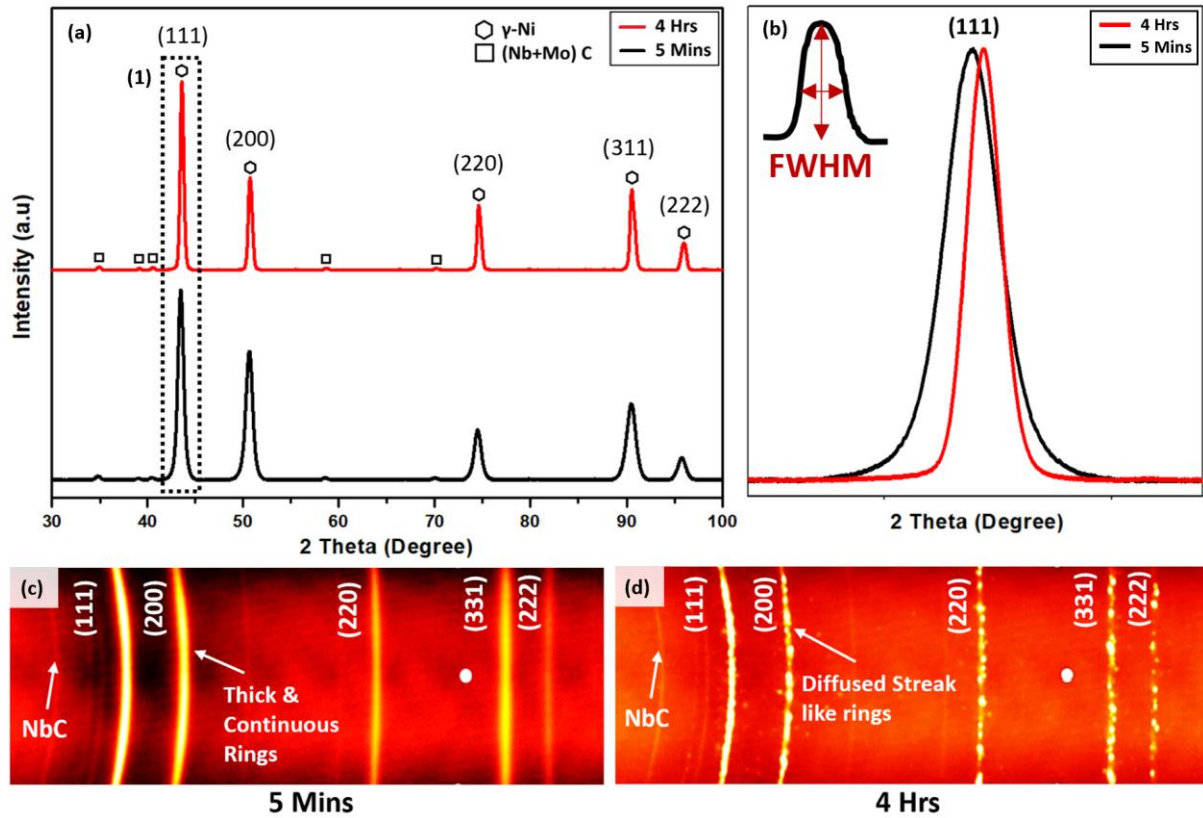


Fig. 5.3: (a) XRD of 5 mins and 4 hrs sintered samples; (b) Enlarged view of (111) peak from (a), Debye-Scherrer rings of (c) 5mins and (d) 4 hrs sintered samples.

Fig. 5.3b shows an enlarged view of the (111) peak from Fig. 5.3a, from which it can be seen that the (111) peak in the 5 mins sintered sample has a greater full width at half maximum (FWHM) when compared to the 4 hrs sample, which is due to strain accumulation during the initial stages of particle coarsening during the sintering and the lack of atomic periodicity during the initial stages of diffusion leading to grain boundaries with higher misorientation. As the sintering time increases, the grains try to rotate or rearrange to reduce the misorientation

energy of the system and, thus, the 4 hrs sintered sample has less strain accumulation when compared to the 5 mins sintered sample and a corresponding narrower FWHM [69,78]. Fig. 5.3 (c & d) displays the Debye-Scherrer rings for 5 mins and 4 hrs sintered samples. The rings corresponding to the γ -Ni phase in the 5 mins sample are thick and continuous, which indicates that there is a high dislocation density in the material and the absence of preferential texture formation, respectively. Conversely, the Debye-Scherrer rings of 4 hrs sintered sample are diffuse, streak-like rings which indicate reduced dislocation density, in agreement with the FWHM measurements, and the formation of preferential texture during sintering, where the texture development may be attributed to the rotation or rearrangement of grains to reduce the grain boundary energy during sintering (Fig. 5.3d) [78].

Fig. 5.4a depicts the optical images, SEM backscattered electron (BSE) images, and EDS compositional maps of 5 mins and 4 hrs sintered samples. The precipitation of metal carbides generally takes place in high-energy regions such as along dislocations and grain boundaries [79]. In the 5 mins sintered sample, metal carbides are generally homogeneously distributed at the grain boundaries and in the matrix. Metal carbides in the 4 hrs sintered sample are also formed along the grain boundary regions but are less present within the grains. In both samples the metal carbides are rich in Nb and Mo, as can be seen from the compositional maps in Fig. 5.4a, in which the (Nb+Mo) carbides are generally formed because of low solubility limits of Nb in the Ni-matrix at higher temperatures and favourable free energy conditions for forming NbC type intermetallics due to solute segregation [77,80]. The distribution of metal carbides in the 4 hrs sintered sample is heterogeneous in nature. During the long-term sintering (i.e., 4 hrs), the initially formed metal carbides that were homogeneously distributed tend to coarsen due to the availability of excess Nb solute in the matrix and generally tend to coarsen near the grain boundaries.

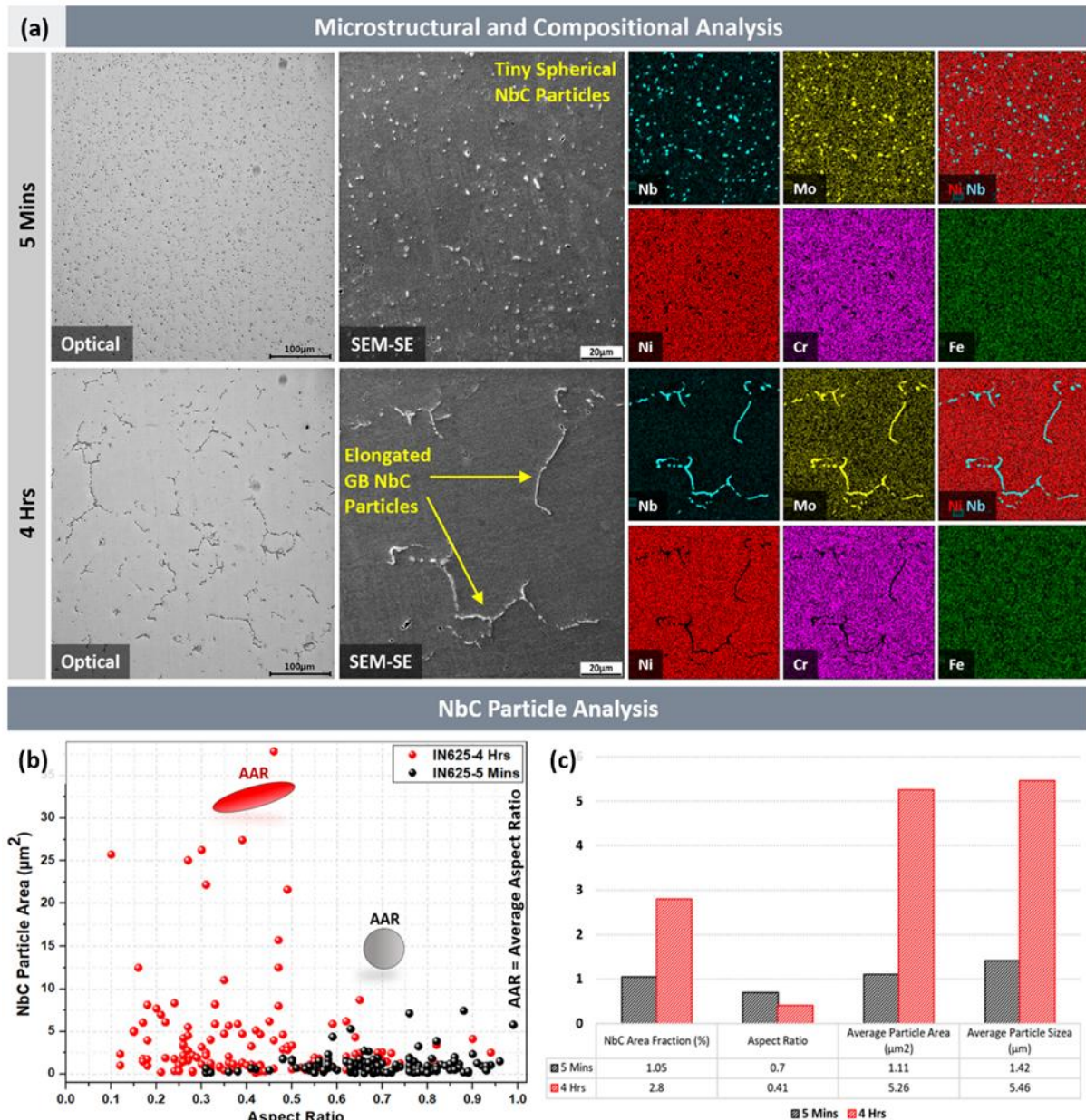


Fig. 5.4: (a) Optical microscopy, SEM-BSE, and EDS elemental maps of 5 mins and 4 hrs sintered samples; (b) NbC particle area vs. aspect ratio map, with the average aspect ratio (AAR) of each particle schematically shown, (c) NbC particle analysis comparison between 5 mins and 4 hrs sintered samples.

The (Nb+Mo)C particle area vs aspect ratio is plotted in Fig. 5.4b. The metal carbides in 5 mins sintered samples have a lower particle area and higher aspect ratio than the metal carbides of 4 hrs sintered samples, indicating the higher sphericity of the metal carbides in the 5 mins sample.

Conversely, the lower aspect ratio of the carbide particles in the 4 hrs sample indicates they are more elongated, and also have a larger average particle area. The particle analysis from both samples is depicted in Fig. 5.4c, from which it can be seen that the average area fraction of (Nb+Mo)C particles is higher in the 4 hrs sintered sample (2.8 %) when compared to the 5 mins sintered sample (~1 %), and the average (Nb+Mo)C particle area and size of 4 hrs sintered sample is comparatively higher than the 5 mins sintered sample (5.26 vs. 1.11 μm^2), which indicates the metal carbide coarsening in the 4 hrs sintered sample is due to solid state diffusion. The small, homogeneously distributed metal carbides in the 5 mins sintered sample are advantageous in improving the strain-hardening capabilities of the alloy by pinning the dislocations, while the coarse and elongated grain boundary metal carbides in the 4 hrs sintered sample have been noted to slow grain boundary migration at higher temperatures and help to retain high-temperature strength [81].

5.3 Grain Analysis

Fig. 5.5 presents the orientation maps of the 5 mins and 4 hrs sintered samples. The orientation gradient in the grains of the 5 mins sintered sample indicates the heterogeneous strain accumulation caused during grain coalescence. Conversely, the orientation gradient is reduced in the 4 hrs sintered sample, which is attributed to the time available for preferential orientation and growth of grains with longer sintering times. A higher number of twins are present in the 5 mins sintered sample. Nickel-based superalloys fall in the category of medium-stacking fault energy, which aids in the formation of annealing twins when exposed to high temperatures, such as during sintering [82]. It is also noticeable that the 4 hrs sintered sample has fewer number of twin boundaries compared to the 5 min sintered sample, but the twins in the 4 hrs sample are coarser, which indicates the grain growth and coalescence of the twin boundaries with increasing sintering time [78].

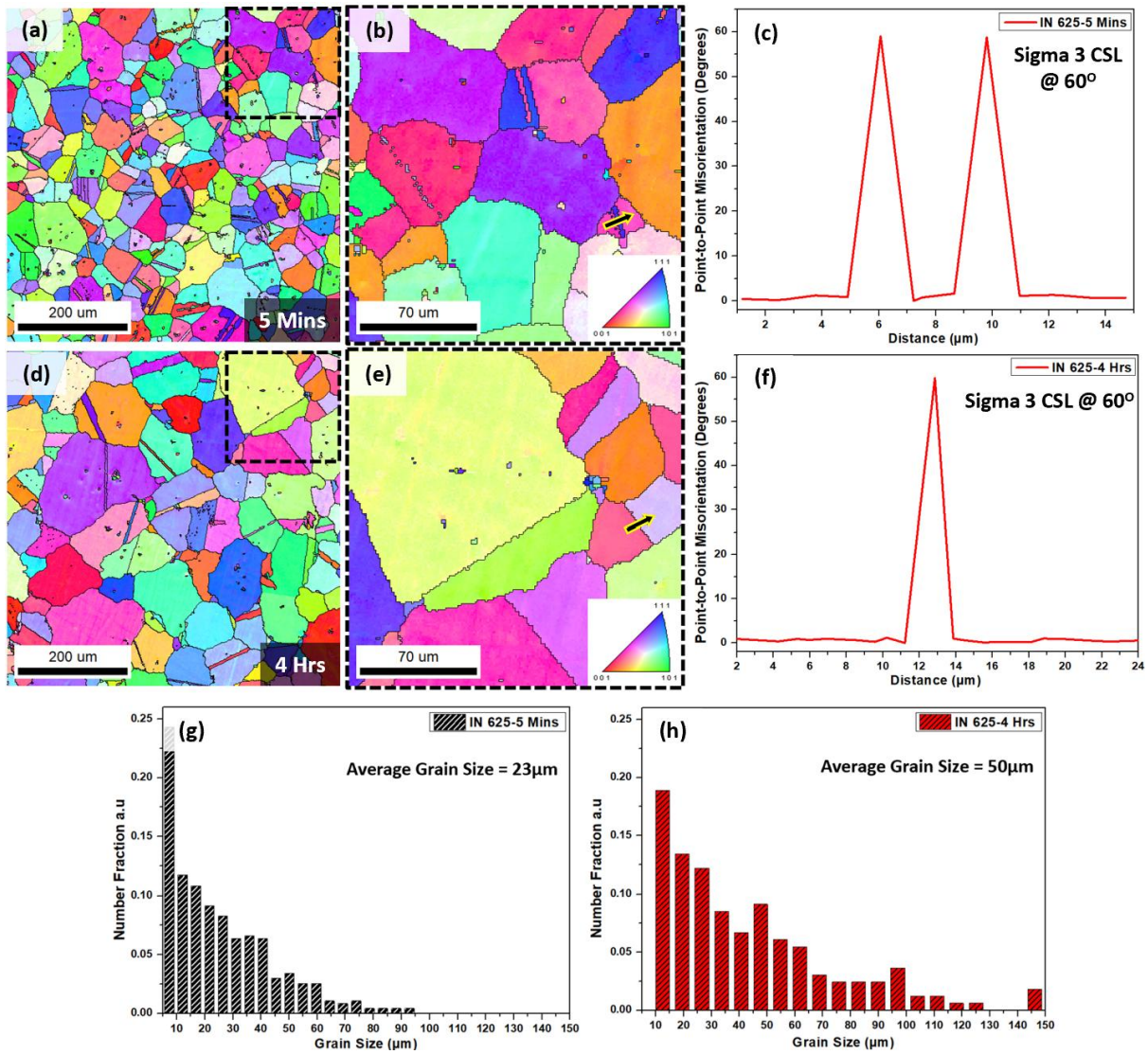


Fig. 5.5: (a & d) Orientation maps of (a) 5 mins and (d) 4 hrs sintered samples taken perpendicular to the build direction; (b & e) Enlarged orientation maps with point-to-point misorientation plot depicting the Sigma 3 CSL for (b) 5 mins and (e) 4 hrs sintered samples; (g & h) Grain size histogram of (g) 5 mins and (h) 4 hrs sintered samples.

Fig. 5.5 (b & e) presents enlarged orientation maps from Fig. 5.5 (a & d), respectively, with a point-to-point misorientation taken across twin boundaries for 5 mins and 4 hrs sintered samples (ref. Fig. 5.5 (c & f), respectively). The twin boundaries are seen to have distinct misorientations at $\sim 60^\circ$, corresponding to coincident site lattice (CSL) $\Sigma 3$ boundaries, which generally have a misorientation of $60^\circ/[111]$ and are well known as coherent twin boundaries

[83]. The formation of twin boundaries in Ni-based superalloys is known to increase the strain-hardening capabilities of the alloy without sacrificing the ductility [84]. Fig. 5.5 (g & h) denotes the grain size distribution of 5 mins and 4 hrs sintered samples, respectively. The grains are larger in the 4 hrs sintered sample ($\sim 50\ \mu\text{m}$) when compared to the 5 mins sintered sample ($\sim 23\ \mu\text{m}$), due to the grain coarsening when exposed at elevated temperatures for prolonged times (i.e., 4 hrs sintering).

5.4 Mechanical Properties

Fig. 5.6 (a & b) depicts the engineering stress-strain curves and summary of the tensile properties of the 5 mins and 4 hrs sintered samples, from which it can be seen that the 4 hrs sintered samples had higher ultimate tensile strength, yield strength, and elongation compared to the 5 mins sintered sample. The level of strain hardening is also higher in 4 hrs sintered samples when compared to the 5 mins sintered sample.

Fractography of the 5 mins and 4 hrs sintered samples is depicted in Fig. 5.6 (c and d), respectively. The 5 mins sintered sample fractography shows a micro-void coalescence (Fig. 5.6c1), indicating the ductile failure. Some cracks were also visible near the porosity (Fig. 5.6c2); porosity has been seen to induce localised strain, which can lead to preferential crack initiation sites [85]. The stress intensification near the cracks caused microscopic cleavage fracture, indicated by yellow arrows in Fig. 5.6c2. The fractography analysis of the 4 hrs sintered sample has shown a ductile failure as indicated by micro-void coalescence. However, evidence of micro-cracks can still be observed on the fracture surface in Fig. 5.6d2. This can be attributed to the incompatible deformation between the Ni-matrix and (Nb+Mo)C, and the interface between the matrix and carbide acts as a crack initiation site [86].

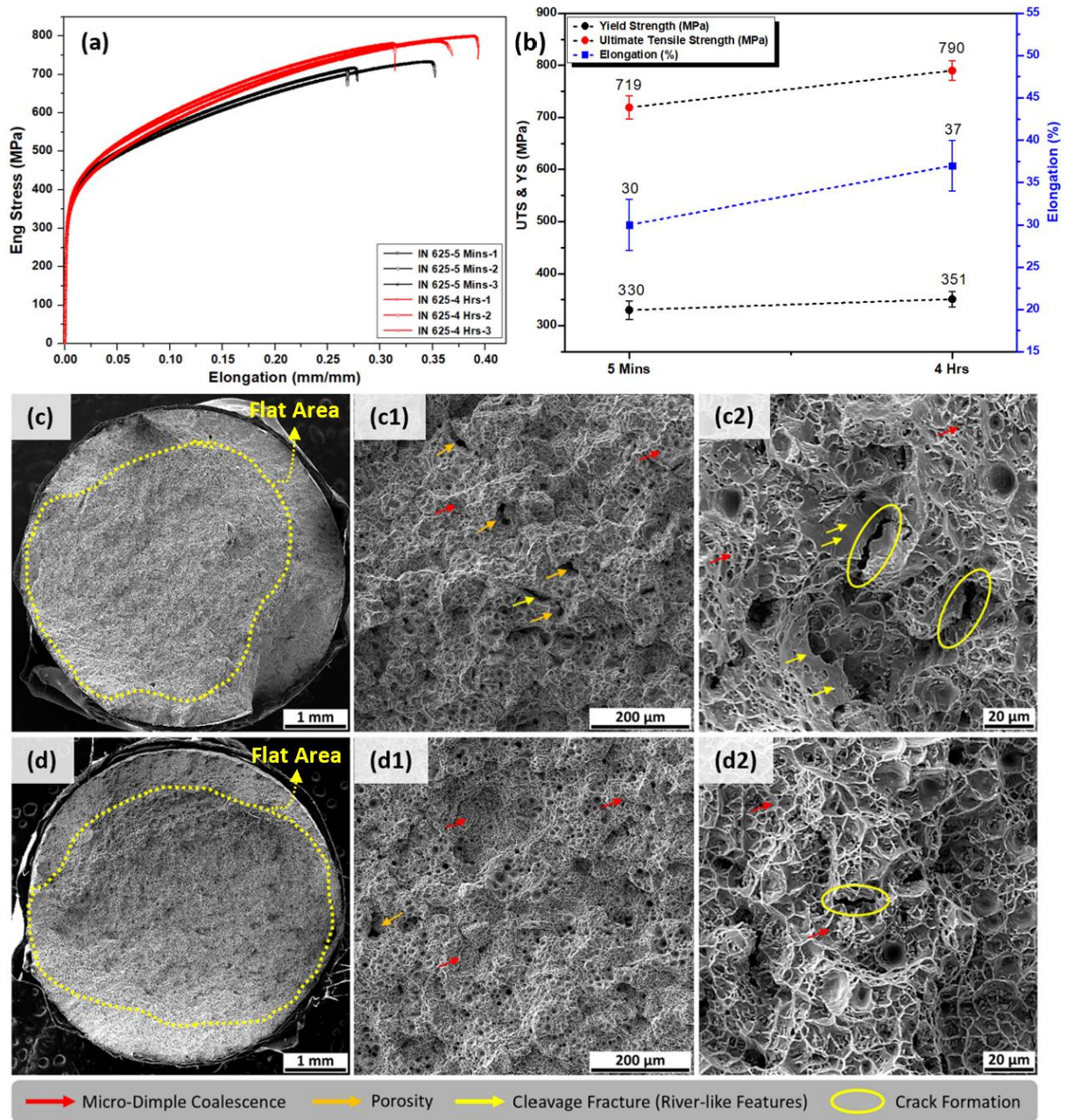


Fig. 5.6: (a) Tensile stress-strain curves of 5 mins and 4 hrs sintered samples, (b) Summary of the average yield strength, ultimate strength, and elongation of 5 mins and 4 hrs sintered samples, (c) Fractography of 5 mins sintered sample and (d) Fractography of 4 hrs sintered sample.

Chapter 6

6. Discussion

6.1 Microstructural Evolution and Property Correlation

Microstructure evolution and densification in metal extrusion additive manufacturing are mostly driven by the sintering kinetics [86]. Fig. 6.1 schematically illustrates the sequential microstructure evolution from powder to sintered samples within the current study. Initially, the paste is deposited on the substrate in the required shape, and it is set to dry. This printed part, without any post-processing, is called the green part and lacks the required strength and is easy to break. To improve the strength, the green part is sintered. In this work, the green part was sintered for 5 mins and 4 hrs at 1290 °C.

The different stages of atomic diffusion during sintering play a crucial role in the densification of the samples [87]. Typically, there are three types of diffusion (grain boundary, surface, and volumetric diffusion). At higher temperatures, volumetric diffusion plays a crucial role in the final densification of the samples [78,83]. Both the samples were subjected to high-temperature sintering (i.e. 1290 °C) where the volumetric diffusion is dominant but the time available for sintering also plays a greater role in the atomic diffusion, hence it was seen that the 4 hrs sintered sample had a higher densification due to the higher volumetric atomic diffusion when compared to the 5 mins sintered sample. As there was a longer sintering time for the 4 hrs sample, the microstructural features such as grain size, CSL boundaries, and carbides were comparatively larger than the 5 mins sintered sample.

The mechanical properties of both samples were comparable, although the 4 hrs sintered samples consistently had greater strength and ductility, despite possessing distinctly different microstructures. The near similar tensile strength in the 5 mins sintered sample can be attributed to the homogeneously distributed carbides, finer grain structure, and high fraction of twin

boundaries, which are known to strengthen the material and give higher tensile properties. However, due to a higher amount of porosity in the 5 mins sintered samples, there was a detrimental effect on the ductility. On the other hand, the 4 hrs sintered sample showed a better strength-ductility trade-off due to higher densification and lower porosity, despite a coarser grain structure with elongated carbide particles.

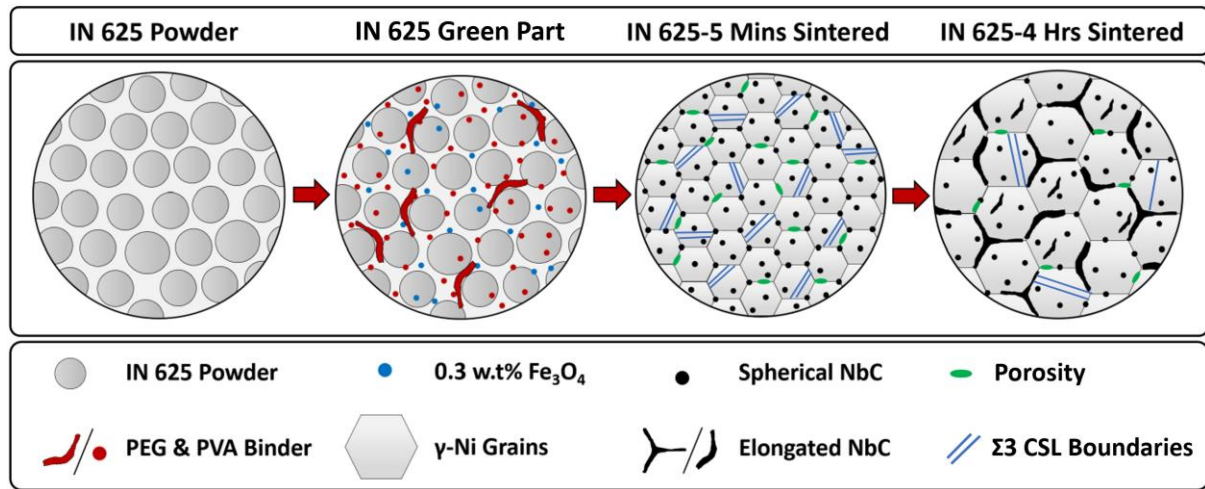


Fig. 6.1: Sequential microstructure evolution from powder to sintered samples

6.2 Effect of Sintering on the Grain Boundary Character Distribution (GBCD)

From the misorientation angle and grain boundary character distribution plots shown in Fig. 6.2 (a & b), the 4 hrs sintered sample has a greater amount of low-angle grain boundaries (LAGB) compared to the 5 mins sintered sample, both samples have a similar fraction of high-angle grain boundaries, and finally, the 5 mins sintered sample contains a greater fraction of twin boundaries ($\Sigma 3$ CSL) compared to the 4 hrs sintered sample. During long-term exposure (i.e., 4 hrs) at high temperatures, volumetric atomic diffusion tends to increase the LAGB and reduce the twin boundaries by grain boundary mobility, coalescence, and coarsening [69,78,83]. The boundary near the A end of the arrow in Fig. 6.2 (c) denotes a $\Sigma 9$ CSL with a misorientation of 38.2° and the boundary near the B end of the arrow indicates a $\Sigma 3$ CSL (twin)

with a misorientation of 59.8° . The $\Sigma 3$ CSL boundaries tend to coarsen in the 4 hrs sintered sample, and the coalescence of two $\Sigma 3$ CSL boundaries tends to produce $\Sigma 9$ CSL boundaries (i.e., $\Sigma 3 + \Sigma 3 = \Sigma 9$) [88–90]. Fig. 6.2 (c) illustrates the enlarged orientation map of the 4 hrs sintered sample and a corresponding point-to-point misorientation plot taken along the black arrow. It is much more evident that one grain consists of $\Sigma 3$ CSL and $\Sigma 9$ CSL boundaries and can be attributed due to the coalescence of $\Sigma 3$ CSL boundaries due to the longer time for diffusion in the 4 hrs sintered sample.

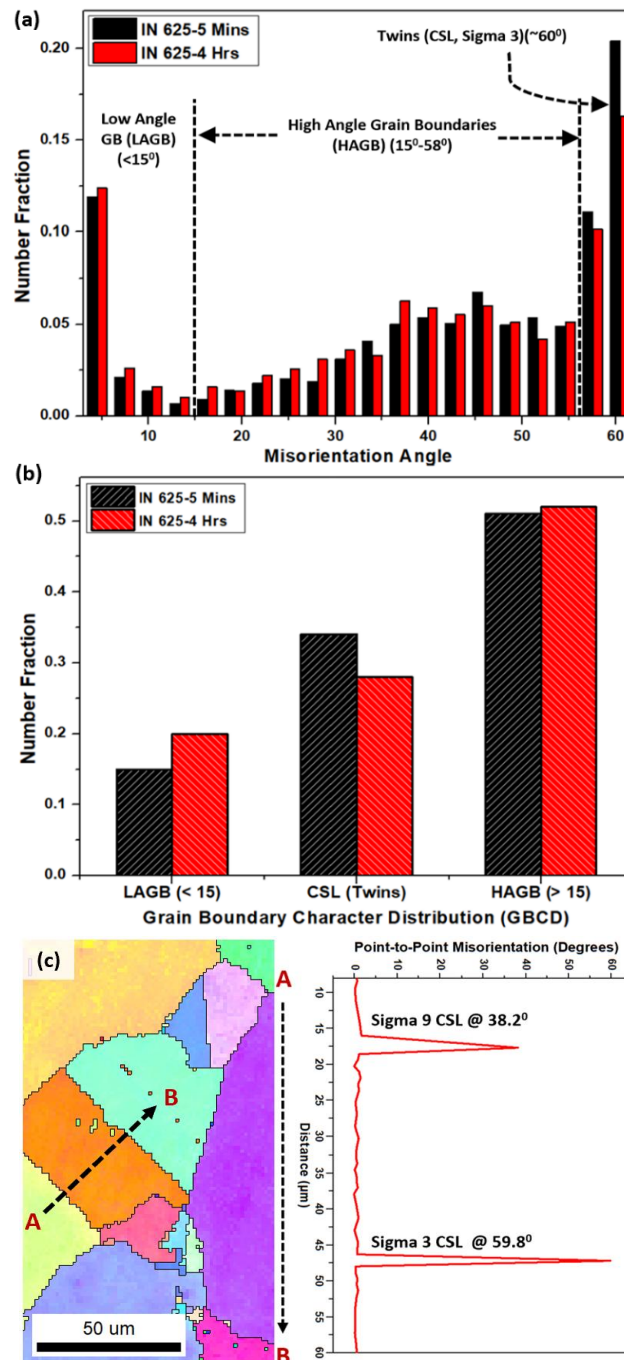


Fig. 6.2: (a) misorientation angle distributions within Inconel 625 samples sintered for 5 mins and 4 hrs, (b) grain boundary character distribution chart of Inconel 625 samples sintered for 5 mins and 4 hrs, (c) enlarged orientation map of 4 hrs sintered sample with a point-to-point misorientation map taken along the arrow (A to B)

Although the 5 mins sintered sample exhibited higher porosity compared to the 4 hrs sample, its strength and ductility were only slightly lower (see Fig. 5.6 (a & b)). This relatively good mechanical performance can be attributed to its higher fraction of $\Sigma 3$ twin boundaries, which are known to enhance mechanical properties by reducing grain boundary energy and improving boundary cohesion, thereby impeding crack initiation and intergranular fracture. In contrast, the 4 hrs sintered sample exhibited a slightly higher fraction of low-angle grain boundaries (LAGBs), which are generally associated with improved ductility due to their ability to accommodate dislocation glide with minimal resistance. Meanwhile, high-angle grain boundaries (HAGBs) contribute to strengthening by acting as effective dislocation barriers but may also promote strain localisation and reduce ductility. Therefore, the observed mechanical behaviour results from a complex interplay between $\Sigma 3$ twin boundaries, LAGBs, and HAGBs, which together govern the strength-ductility trade-off in the sintered samples.

6.3 Texture Evolution

Fig. 6.3 (a & b) presents the inverse pole figure (IPF) triangles of 5 mins and 4 hrs sintered samples extracted from Fig. 5.5 (a & d), respectively, and Fig. 6.3 (c) indicates the (001) IPF triangle standard projections. In the 5 mins sintered sample, there is a random crystallographic orientation with weak intensities near $\langle 001 \rangle$ and a weak fibre of $\langle 331 \rangle$ and $\langle 320 \rangle$. As the sintering time increased, there was an increase in the intensity of the texture in the 4 hrs sintered sample, with the formation of stronger crystallographic texture at $\langle 001 \rangle$, $\langle 331 \rangle$ and a weak fibre near $\langle 211 \rangle$ and $\langle 311 \rangle$. The $\langle 001 \rangle$ texture in the 4 hrs sintered samples denotes the

solidification type of texture of FCC alloys, as $\langle 001 \rangle$ is known to be the easy growth direction [91,92]. The presence of this type of texture may be caused by some liquid phase sintering, given the high homologous sintering temperature, where the atoms tend to diffuse in the less closely packed plane in FCC-based alloys [93]. The possibility of transient liquid state sintering is emphasised by the DSC data in Fig. 4.6 (b), in which the onset of melting for the paste sample was noted to occur at 1293 °C, which is quite near to the sintering temperature. Given that there is $\pm 0.75\%$ error in temperature measurements for the K-type thermocouples that are used to control the furnace temperature, it is possible that localised over-temperatures occurred during the 4 hr hold, potentially leading to transient liquid phase sintering in some regions due to the presence of micron-sized powders. These fine particles, owing to their high surface area and enhanced diffusivity, can exhibit melting point depression, thereby promoting localised necking and densification at elevated temperatures. Similar liquid-state sintering has also been observed in the sintering of Cu [93].

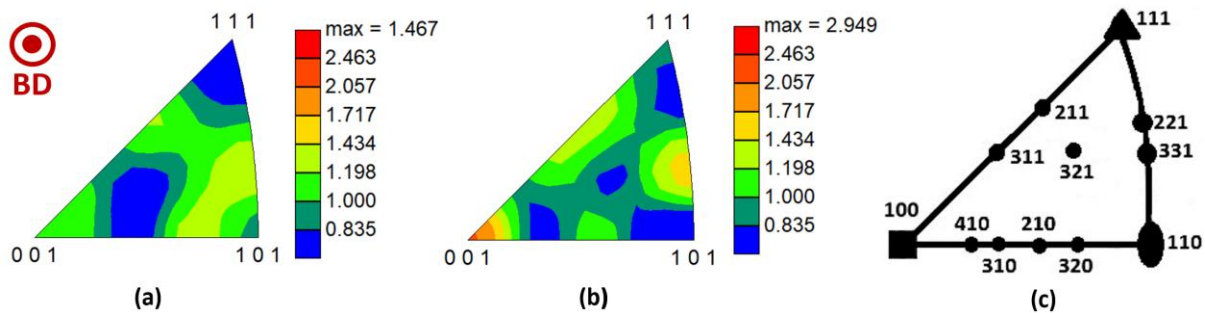


Fig. 6.3: (a & b) IPF triangles representing the texture across the build direction for the (a) 5 min and (b) 4 hr sintered samples, (c) (001) IPF triangle standard projections.

6.4 Effect of Sintering Time on the Crystallographic Parameters

Crystallographic parameters play an important role in determining a material's physical and mechanical properties. While the Debye–Scherrer method can be used to estimate the crystallite size of both samples, it does not account for the strain effect. To assess the impact of

sintering time on both crystallite size and micro-strain, the Williamson-Hall method was employed [94]:

$$\beta \cos \theta = \left(\frac{k\lambda}{D} \right) + 4\epsilon \sin \theta$$

Where β is the Full Width at Half Maximum measured from Fig. 5.3 (b), k is the shape factor constant ($k=0.94$ for cubic materials), λ is the wavelength of Cu K α radiation ($\lambda=0.154\text{nm}$), D is the crystallite size, and ϵ is the micro-strain. Williamson-Hall plots were calculated for 5 mins and 4 hrs sintered samples, and the $\beta \cos \theta$ vs $4\sin \theta$ plots of both the samples are depicted in Fig. 6.4 (a & b). Both sintering times exhibit a negative slope, indicating the presence of compressive strain in both samples. Compressive strain during sintering primarily arises from the shrinkage of the material as it densifies. As pores close and material flows into the voids, the overall volume decreases, resulting in compressive strain due to the stresses acting on the material during sintering. The average crystallite sizes of the samples sintered for 5 mins and 4 hrs are 10.9 nm and 18.2 nm, respectively. This increase in crystallite size with longer sintering times can be attributed to enhanced atomic diffusion and grain boundary movement, which allow smaller crystallites to coalesce and form larger ones. Smaller crystallite sizes tend to promote fine grains, which act as barriers to dislocation motion, increasing the material's strength. Li et al. [95] have also observed that fine crystallite size in a sample which had a smaller grain size. The effect of grain size is discussed in the subsequent section.

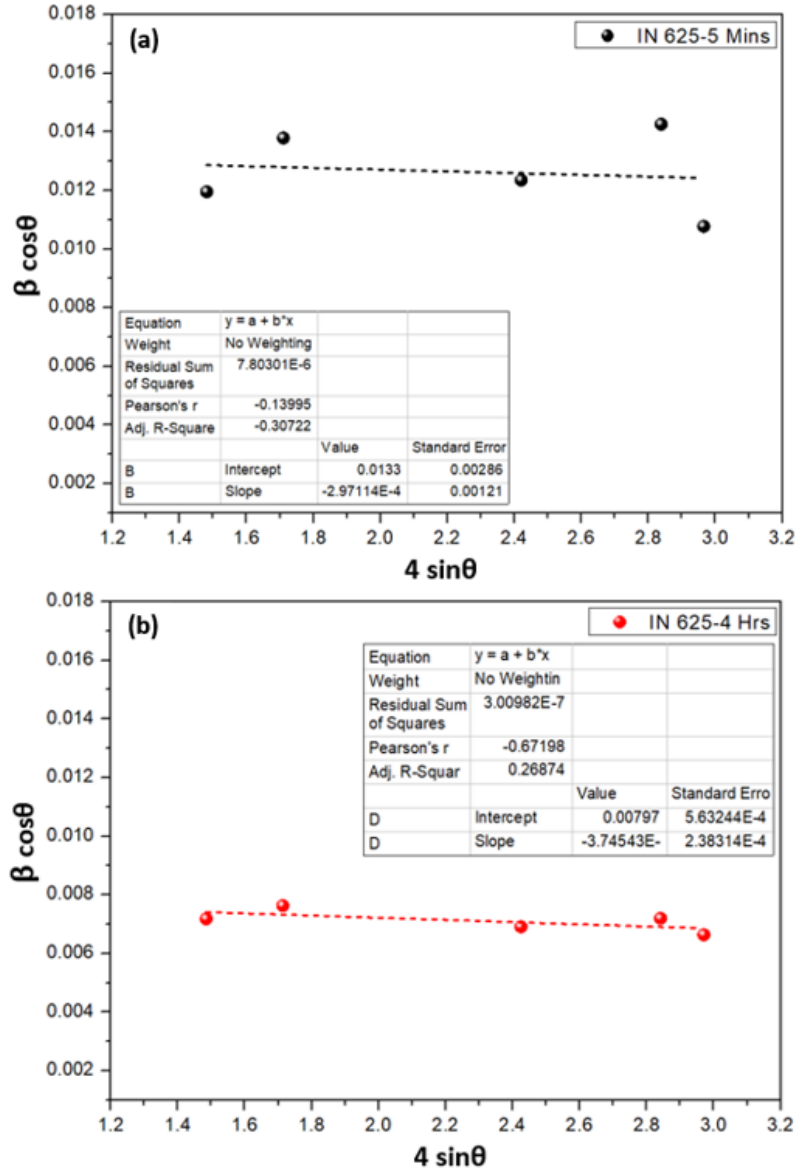


Fig. 6.4: (a & b) Williamson–Hall Plot of 5 mins and 4 hrs sintered samples

6.5 Strengthening Mechanisms

The strengthening mechanisms in Ni-based alloys are primarily influenced by solid solution strengthening ($\Delta\sigma_{ss}$), grain boundary strengthening ($\Delta\sigma_{GB}$), dislocation strengthening ($\Delta\sigma_D$), and precipitation strengthening ($\Delta\sigma_P$). These four factors collectively determine the yield strength of Inconel 625 [96]. A brief overview of each strengthening mechanism, along with the mathematical calculations for samples sintered for 5 mins and 4 hrs, is provided below.

6.5.1 Solid Solution Strengthening ($\Delta\sigma_{ss}$)

Solid solution strengthening in Inconel 625 arises from the presence of niobium (Nb), molybdenum (Mo), and chromium (Cr) in the γ -Ni matrix. The solid solution strengthening in Inconel 625 can be estimated by combining the individual strengthening contributions of each solute element using Roth's model [97]:

$$\Delta\sigma_{ss} = \left(\sum_i k_i^{1/n} \cdot c_i \right)^n$$

Where k_i represents the strengthening constant for each solute and is obtained from literature for various solutes in Ni-matrix, and c_i is the concentration of the solute, with n considered as 1/2 according to the Feltham model [97]. The solute concentrations of 5 mins and 4 hrs sintered samples were estimated from EDS point analysis obtained from the Ni-matrix and are depicted in Fig. 6.5 and Table. 6.1. The solid solution strengthening for the 5 mins and 4 hrs sintered samples is 235.4 MPa and 223.6 MPa, respectively. The reduction in strength observed in the 4 hrs sintered sample is attributed to the absence of Nb and the depletion of Mo in the Ni-matrix, caused by the formation of elongated grain boundary carbides.

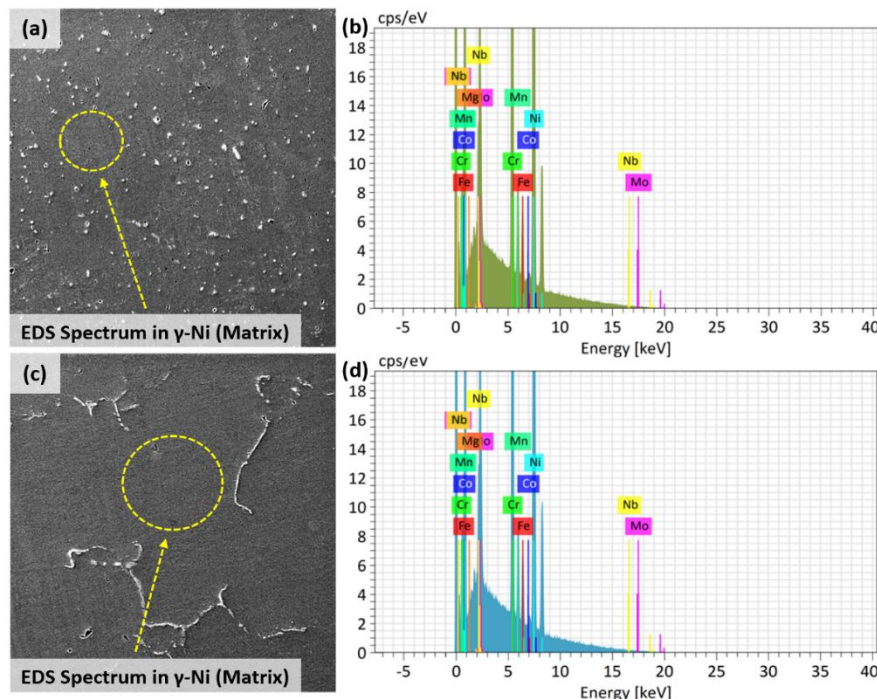


Fig. 6.5: (a & b) SEM-SE image and corresponding matrix EDS spectrum of 5 mins sintered sample, (c & d) SEM-SE image and corresponding matrix EDS spectrum of 4 hrs sintered sample.

Table 6.1: Solute concentration, c_i (at. %) for 5 mins and 4 hrs sintered samples collected from EDS spectrum in Ni-matrix and the strengthening constant of different solutes, k_i (MPa at. Fraction^{-1/2}) in Ni-matrix [97]

Element	Cr	Fe	Mo	Nb	Mn
Solute Concentration (5 mins)	27.6	3.4	2.1	0.092	0.17
Solute Concentration (4 Hrs)	27.7	3.5	1.7	0	0.15
Strengthening Constant (MPa at. Fraction^{-1/2})	337	153	1015	1183	448

6.5.2 Grain Boundary Strengthening ($\Delta\sigma_{GB}$)

The grain boundaries in the material serve as barriers to dislocation motion, with a smaller grain size providing more barriers and thereby enhancing the material's strength. As shown in Fig. 5.5, both samples contain twin boundaries, which are a form of special high-angle grain boundaries, and exhibit similar resistance to dislocation motion. Therefore, the combined effect of grain boundaries and twins on the material's strength can be estimated using the Hall-Petch relationship [98]:

$$\Delta\sigma_{GB} = kd^{-\frac{1}{2}}$$

Where k is the Hall-Petch coefficient and d is the average grain size. For Ni-based alloys such as Inconel 625, the Hall-Petch coefficient (k) is considered to be 710 MPa. $\mu\text{m}^{1/2}$ [98]. The average grain size, inclusive of twin boundaries, of the 5 mins and 4 hrs sintered samples is shown in Fig. 5.5 (g & h) and was found to be 23 μm and 50 μm , respectively. The calculated

grain boundary strengthening of 5 mins and 4 hrs sintered samples are 148 MPa and 100.4 MPa, respectively.

6.5.3 Dislocation Strengthening ($\Delta\sigma_D$)

The dislocation density in the sample influences the material's strength through dislocation-dislocation interactions, which create barriers that impede further dislocation motion. These interactions can result in the formation of jogs (immobile dislocations) and kinks (mobile dislocations), both of which contribute to the material's strengthening. A higher dislocation density, up to a certain limit, is known to enhance the material's strength. The theoretical strengthening effect of dislocation density can be estimated by using Bailey's model [99]:

$$\Delta\sigma_D = M\alpha_T Gb\sqrt{\rho_{GND}}$$

The Taylor factor (M) is typically considered to be 3 for Ni-based alloys. The material constant α_T is temperature-dependent and given as 0.2 [96]. The shear modulus (G) for Inconel 625 is 76 GPa [100], and the Burgers vector (b) is 0.25 nm. The geometrically necessary dislocation density (ρ_{GND}) in the material can be calculated using the Kernel Average Misorientation (KAM) method, based on the following relation [96]:

$$\rho_{GND} = \frac{2\theta_{KAM}}{xb}$$

In which: θ_{KAM} represents the average KAM value obtained from Electron Backscatter Diffraction (EBSD) analysis, x refers to the unit length, which is twice the step size [96], so the step size of 1.5 μm is used in this study, $x = 3 \mu\text{m}$; and b is the Burgers vector, (0.25 nm) [96]. The KAM plot for the 5 mins and 4 hrs sintered samples is shown in Fig. 6.6. The average θ_{KAM} values for the 5 mins and 4 hrs sintered samples are 0.59° and 0.52° , respectively. The KAM values exceeding 2° were excluded from the calculation based on the assumption that they contribute to the grain boundary strengthening [96]. The geometrically necessary

dislocation density (ρ_{GND}) for 5 mins and 4 hrs sintered samples are then calculated to be $2.8 \times 10^{13} \text{ m}^{-2}$ and $2.4 \times 10^{13} \text{ m}^{-2}$, respectively, resulting in the dislocation strengthening contributions ($\Delta\sigma_{\text{D}}$) for 5 mins and 4 hrs sintered samples of 60.4 MPa and 55.8 MPa, respectively.

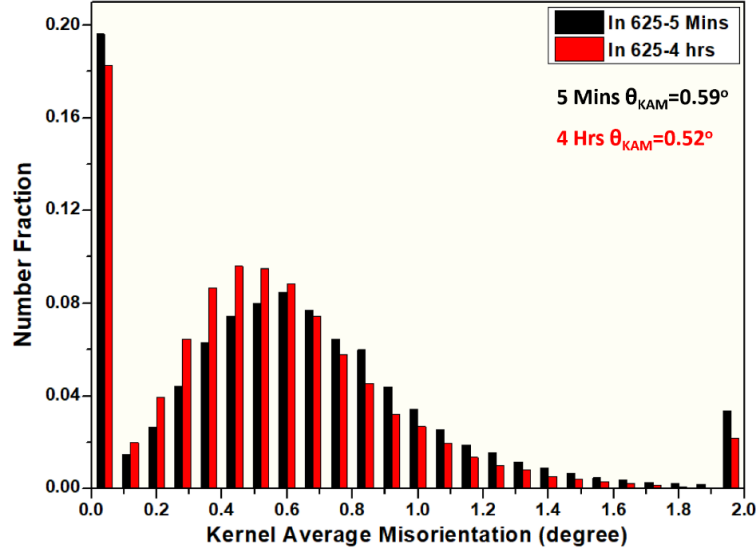


Fig. 6.6: Kernel average misorientation (KAM) plot of 5 mins and 4 hrs sintered samples.

6.5.4 Precipitation Strengthening ($\Delta\sigma_{\text{P}}$)

In the current study, precipitation strengthening occurs through the formation of carbides during the sintering process of Inconel 625. As shown in Fig. 5.4 (a & c), the formation of (Nb+Mo) carbides is observed in both conditions. The average carbide size for the 5 mins and 4 hrs sintered samples is $1.42 \mu\text{m}$ and $5.46 \mu\text{m}$, respectively. Given that the carbide sizes in both samples are in the micron range, the precipitation strengthening primarily occurs through the Orowan looping mechanism as the stress required for precipitate shearing of micron-scale carbides is significantly higher than the stress required for Orowan looping, thus making the Orowan looping mechanism more energetically favourable. Precipitation strengthening of the carbides can be estimated by using the Ashby-Orowan model [101]:

$$\Delta\sigma_{\text{P}} = \left(\frac{0.538 G b f^{\frac{1}{2}}}{x} \right) \ln \left(\frac{x}{2b} \right)$$

Where G is the shear modulus of the γ -Ni matrix ($G=76$ GPa), b is the Burgers vector ($b=0.25\text{nm}$), x is the average size of the carbides, and f is the volume fraction of the carbides. The volume fraction of carbides in 5 mins and 4 hrs sintered samples are 1.05% and 2.8%, respectively. The estimated precipitation strengthening contribution in 5 mins and 4 hrs sintered samples are 6 MPa and 2.9 MPa, respectively. The contribution of precipitation strengthening is relatively low due to the coarse nature of the carbides. It can also be concluded that a γ -Ni-matrix without carbides will be beneficial in improving the strength of the alloy through the solid solution strengthening effect.

6.5.5 Contribution of Various Strengthening Mechanisms

The cumulative effect of each strengthening mechanism and the variation between the theoretical and experimental yield strength of the 5 mins and 4 hrs sintered samples is shown in Fig. 6.7. Theoretical calculations suggest a higher overall yield strength for the 5 mins sintered sample compared to the 4 hrs sintered sample, primarily due to grain boundary strengthening. Additionally, solid solution strengthening, dislocation strengthening, and precipitation strengthening show a slightly greater effect in the 5 mins sintered sample than in the 4 hrs sintered sample. However, the experimental results display an opposite trend, in which the 4 hrs sintered samples exhibit a higher average yield strength than the 5 mins sintered samples.

The discrepancy between the experimental and theoretical yield strengths can be assessed using the yield ratio:

$$Yield\ Ratio = \frac{YS_{Experimental}}{YS_{Theoretical}}$$

The yield ratios for the 5 mins and 4 hrs sintered samples are 73.4% and 91.8%, respectively. The 8.2% deviation observed in the 4 hrs sintered sample is generally acceptable; however, the 26.6% deviation in the 5 mins sintered sample is considered significant. This large discrepancy in yield strength can be primarily attributed to the higher fraction of elongated porosity present in the 5 mins sintered sample. The degradation of properties due to elongated pores has not been considered in the strengthening calculations. Moreover, the grain size used here includes twins, which may lead to an overestimation of grain boundary strengthening. Consequently, the theoretical estimation of yield strength in the 5 mins sintered sample may be overpredicted. All the microstructure features in the 4 hrs sintered sample (i.e., coarser grains, elongated & larger NbC) should lead to reduced mechanical properties, but the fact that the strength & ductility are greater than the 5 min sample suggests that the mechanical properties are still largely dictated by porosity closure.

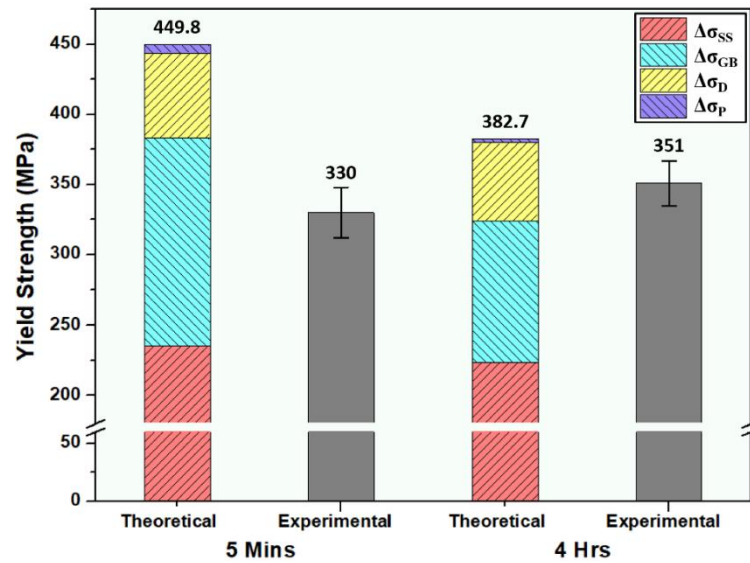


Fig. 6.7: Summary of strengthening mechanism contributions and comparison of theoretical and experimental yield strength of 5 mins and 4 hrs sintered samples

It can be concluded that the experimental yield strength is strongly influenced by the material's density. While the discrepancy in the experimental yield strength between the 5 mins and 4 hrs sintered samples is approximately 20 MPa, the discrepancy in the ultimate tensile strength

increases to about 70 MPa (ref. Fig. 5.6 (b)). This highlights the significant role of density and defect fraction in determining the mechanical behaviour of sintered Inconel 625.

6.6 Ashby Plot

The strength vs. ductility trade-off data collected from conventional and various AM processes, including the samples from the current study, are presented in the Ashby plot in Fig. 6.8 (a & b). Fusion-based AM processes such as L-PBF and L-DED generally exhibit superior mechanical properties when compared to solid-state AM processes, as can be seen in Fig. 6.8 (a). The fusion-based AM processes typically produce hierarchical microstructures (e.g., refined grains, solidification cellular structure, preferential texture, fine intermetallics) during solidification, which tends to increase the strain hardenability of the material by creating barriers for dislocation movement [102–104]. On the contrary, the electron beam melted (EBM) Inconel 625 has properties similar to the solid-state AM of Inconel 625. The powder in EBM is at elevated temperatures, which reduces the cooling rates and promotes grain coarsening [105]. In terms of solid-state AM processes (Fig. 6.8 (b)), additive-friction stir processing (AFSP) of Inconel 625 has shown superior strength, owing to fine-grained structures and breakdown of coarse intermetallics [106,107]. The mechanical properties of Inconel 625, as reported by Desktop Metal and Rapidia for their metal extrusion-based processes, have shown lower strength and ductility when compared to the current study. Similarly, Markforged (Bound Powder Filament) has reported greater elongation but lower strength than the samples in the current study. From Fig. 6.8 (b), it can be seen that the current study is at the leading edge of the strength-ductility trade-off curve for solid-state AM of Inconel 625. Metal Extrusion AM has a lower processing cost compared to laser- or electron beam-based AM. Its feasibility is higher than that of fusion-based counterparts because it does not require expensive and hazardous melting sources such as lasers, arcs, or electron beams.

However, since Metal Extrusion AM combines printing and sintering, the overall processing time is generally longer than that of fusion-based AM technologies.

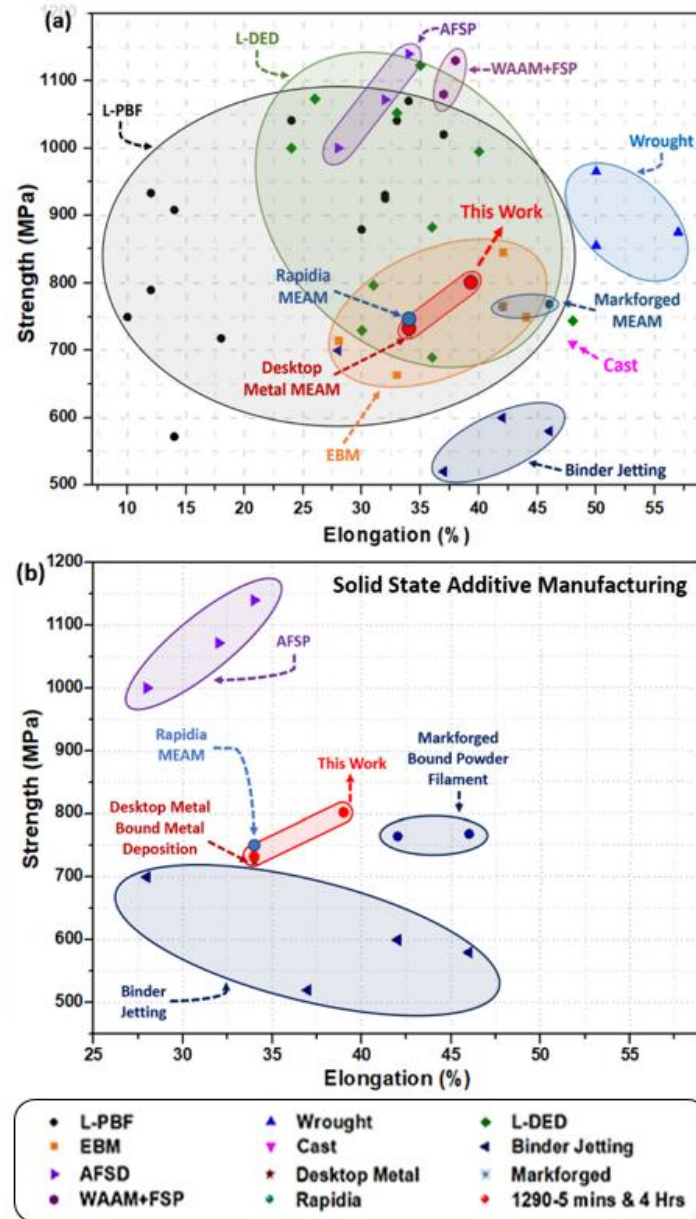


Fig. 6.8: (a) Ashby plot indicating the strength vs. ductility data collected from conventional manufacturing and various AM processes such as L-PBF [47, 108–113], L-DED [110,114–118], EBM [119–122], FSP [106,115,124], WAAM+FSP [125], cast [126], and wrought [127,128], (b) Ashby plot indicating the strength vs ductility data collected from various solid-state AM processes compared to the current study, binder jetting [121,129], metal extrusion/metal filament-based processes [72, 130–132].

Chapter 7

7. Conclusions and Future Works

7.1 Conclusions:

This study systematically investigated the critical influence of sintering time on the process-structure-property relationship of Inconel 625 fabricated via Metal Extrusion Additive Manufacturing (MEAM). The findings highlight that sintering duration at high homologous temperatures is a pivotal parameter in achieving optimal densification and mechanical performance. Specifically, extending the sintering time from 5 mins to 4 hrs at 1290 °C significantly improved densification, leading to a relative density of approximately 99.5%. This enhanced densification was the primary driver for the superior tensile strength and elongation observed in the 4 hrs sintered samples, effectively mitigating the detrimental effects of residual porosity.

Microstructural analysis revealed distinct carbide morphologies and distributions influenced by sintering time. The shorter sintering duration resulted in finer, homogeneously distributed (Nb+Mo)-rich spherical carbides, along with a finer grain structure and a higher fraction of strengthening twin boundaries. Conversely, the extended sintering time promoted the coarsening and elongation of carbides, primarily at grain boundaries, alongside significant grain growth and the development of a strong crystallographic texture along the $\langle 001 \rangle$ direction. This texture evolution, potentially linked to transient liquid phase sintering, suggests complex atomic rearrangement mechanisms at play.

Despite the microstructural features in the 4 hrs sintered samples (coarser grains, elongated carbides) that would typically degrade mechanical properties, their superior densification proved to be the dominant factor in achieving enhanced strength and ductility. The 5 mins sintered samples, while exhibiting lower overall mechanical performance due to higher

porosity, demonstrated that their refined microstructural characteristics provided a moderating effect, retaining a reasonable level of mechanical integrity. This underscores a crucial strength-ductility trade-off, while beneficial microstructural features can contribute to strength, their impact is significantly overshadowed by the presence of porosity. The study's results position MEAM-processed Inconel 625 at the leading edge of the strength-ductility trade-off curve for solid-state additive manufacturing, demonstrating its potential as a viable alternative to fusion-based techniques for crack-susceptible Ni-based superalloys.

7.2 Future Works:

Building upon the insights gained from this study, several avenues for future research are proposed to further optimise the MEAM of Inconel 625 and enhance its applicability:

1. **Systematic Sintering Parameter Optimisation:** While this study focused on two distinct sintering times, future work should involve a more comprehensive parametric study of sintering temperature, heating/cooling rates, and atmosphere. A design of experiments (DoE) approach could be employed to establish a robust process window that maximises densification while controlling undesirable microstructural evolution.
2. **Detailed Investigation of Transient Liquid Phase Sintering:** The observation of $\langle 001 \rangle$ texture development in the 4-hour sintered sample suggests the possibility of transient liquid phase sintering. Further in-depth analysis using advanced characterisation techniques (e.g., in-situ high-temperature XRD or TEM) is needed to confirm the presence and quantify the extent of liquid phase formation and its precise role in densification and texture evolution.
3. **Mechanical Property Anisotropy:** The current study focused on uniaxial tensile properties. Future work should investigate the anisotropic mechanical behaviour (e.g., tensile properties in different build directions, fatigue, and creep resistance) of MEAM-

fabricated Inconel 625, as anisotropy is a common characteristic of additively manufactured parts.

4. **Influence of Binder System and Powder Characteristics:** Explore the impact of variations in binder composition, powder particle size distribution, and powder morphology on green part integrity, debinding efficiency, and subsequent sintering behaviour. This could lead to further improvements in final part density and mechanical properties.
5. **Post-Sintering Heat Treatments:** Investigate the effect of various post-sintering heat treatments (e.g., solutioning and aging) on the microstructure and mechanical properties of MEAM-fabricated Inconel 625. This could enable further optimisation of strength, ductility, and other critical properties by controlling precipitation and grain structure.
6. **Corrosion and Oxidation Resistance:** Given Inconel 625's applications in harsh environments, future studies should assess the corrosion and oxidation resistance of MEAM-processed parts, particularly in relation to residual porosity and carbide characteristics.

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