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Publication Date

2025-12-12

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA

Los Angeles

Advanced Characterization of Deformation Mechanisms
in Additively Manufactured Metallic Systems

A dissertation submitted in partial satisfaction
of the requirements for the degree Doctor of Philosophy
in Materials Science and Engineering

by

Alberico Talignani

2025

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ABSTRACT OF THE DISSERTATION

Advanced Characterization of Deformation Mechanisms

in Additively Manufactured Metallic Systems

by

Alberico Talignani

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2025

Professor Yinmin Wang, Chair

Advances in metal additive manufacturing (AM) are reshaping the design of structural alloys with exceptional performance. This dissertation investigates the deformation behavior of laser powder-bed-fusion (L-PBF) metals through in-situ synchrotron X-ray diffraction (SXRD) and electron microscopy, establishing a mechanistic framework that connects AM-induced microstructures to strength and ductility.

The first part of this work addresses the printability barrier in refractory metals. To our current knowledge, we demonstrate the first near-fully dense, crack-free L-PBF tungsten-based alloy by introducing a small boron addition (0.3 wt.%). This modification disrupts solidification-cracking pathways and enables unprecedented tensile ductility at 800 °C in a material historically viewed as unprintable and intrinsically brittle. These findings establish a new foundation for refractory AM alloys in fusion and extreme-environment applications.

The second part focuses on a TiC-inoculated Al-Mg-Zn-Cu alloy designed for high performance. TiC nanoparticles provide solidification control, producing an equiaxed fine-grained structure that remains stable through post-processing. Hot isostatic pressing (HIP) and T6 aging create a hierarchical precipitation architecture consisting of a grain-boundary MgZn_2 cage and dense intragranular η' /cluster networks. In-situ SXRD measurements of lattice-strain deviation, peak broadening, and diffraction-intensity changes reveal how plasticity initiates and load progressively transfers between the matrix and its precipitates. These mechanisms yield a rare strength–ductility synergy, resulting in the highest specific ultimate tensile strength (SUTS) reported for any aluminum alloy (269MPa/g/cm^3)—exceeding even conventional Ti-6Al-4V.

Complementary SXRD studies of pure Cu, equiatomic CoCrNi, and 316L stainless steel provide a reference framework for interpreting defect evolution in face-centered cubic (FCC) AM metals. Cu enables unambiguous quantification of dislocation-controlled hardening, whereas CoCrNi and 316L illustrate the influence of stacking-fault energy (SFE) on lattice-strain deviation and reflection-dependent behavior. Together with Al, these comparisons show that SXRD response cannot be universally interpreted without accounting for intrinsic elastic properties, SFE, slip-system accessibility, and defect character.

Overall, this dissertation demonstrates that in-situ SXRD is uniquely capable of revealing microstructural load sharing and defect evolution under realistic operating conditions. Coupled with AM-specific microstructure design strategies—from nanoparticle-stabilized grain refinement in Al to boron-driven solidification control in W-B—these results define a pathway for engineering the next generation of lightweight and extreme-environment structural materials.

The dissertation of Alberico Talignani is approved.

Xiaochun Li

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Jenn-Ming Yang

Yinmin Wang, Committee Chair

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2025

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Acknowledgements

I want to thank all the wonderful people who have helped and supported me over the past five years. First, I would like to express my appreciation for my advisor, Professor Yinmin Morris Wang. His passion for science, integrity, and attention to detail have without a doubt shaped my critical thinking skills, view of the scientific world, and overall direction of my life. I am grateful for his support.

Thank you to the members of my Ph.D. committee as well: Prof. Xiaochun Li, Prof. Jaime Marian, and Prof. Jenn-Ming Yang, their insight and suggestions played an important role in improving and structuring this dissertation.

I am incredibly lucky to have worked with great labmates in the past five years. Thank you Dr. Yu-Keng Lin, Cliff Yu, Cindy Wang, Jasmine Yang, and Mengchen Li for making this experience memorable—I will miss you guys a lot.

This dissertation would not have been possible without the help of many collaborators. I would like to thank Dr. Jianchao Ye and Philip DePond at Lawrence Livermore National Laboratory (LLNL) for all their work on tungsten printing and for valuable discussions. Dr. Thomas Voisin and Dr. Jean-Baptiste Forien's help at LLNL was crucial in the early stages of learning SXR, and their insights were greatly appreciated. Thanks to Dr. Tim Groening for doing a wonderful job coordinating the tungsten project over the years. His insight and help with FIB, TEM, knowledge of refractory metals and SXR were invaluable. Thank you to Professor Jianwei Miao and Dr. Haozhi Sha for their insight and help with TEM data collection, as well as to Professor Zan Li for providing additively manufactured Cu materials. A special thank you to

Tianqi Zheng, for all his work printing and optimizing the AA7075 materials that were central to this research.

A big thank you to Dr. Bijun Xie and Professor Penghui Cao at UCI. Your support with TEM characterization was outstanding. I look up to the quality of your research and your work ethic. The conversations we had were always inspiring and exciting.

To my parents, Patrizia Rapis and Luigi Talignani, and my relatives: vi ringrazio di cuore per tutto il vostro supporto, sia negli ultimi cinque anni che da quando mi sono trasferito negli Stati Uniti. Nonostante la distanza, ho sempre potuto contare su di voi. Vi voglio un mondo di bene.

To my brilliant wife, Zoey Anna Brown, who helped me through some of the most critical stages of this doctoral program: You were by my side at my lowest points and never hesitated to do everything you could to help me. I am forever grateful for your support through the long hours in lab, and for talking me through worries and concerns countless times. I would not be where I am today without you. Your motivation and passion inspire me every day. I cannot wait to spend the rest of my life with you.

Lastly, a huge thanks to all my friends—you made this journey an incredible adventure. Despite starting this Ph.D. in 2020, you turned the past few years into some of the best so far!

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Chapter 1. Introduction

1.1 Background

For millennia human society has relied on materials available in nature to create tools needed for survival. From the metal ages to the age of space travel, technological advancement has been closely tied to society's knowledge and application of different materials [1]. Two factors have never been changed since the first tool was manufactured: custom made components are always in demand, and their efficacy is directly related to the degree of control of their properties.

This work sheds light on both aspects. First, it explores the advantages of additive manufacturing (AM), such as its outstanding freedom of design and microstructural engineering. Second, it makes use of state-of-the-art characterization technology to investigate and explain the mechanics of AM materials. Leveraging high-resolution microscopy and synchrotron x-ray facilities, this work relies on atomic-scale imaging and the ability to probe deviations in atomic positions on the order of a fraction of a percentage to push the boundaries of material understanding.

1.2 Additive manufacturing

AM has recently become a popular and promising manufacturing technique that allows for fast, customizable, and highly precise production of components [2–5]. Fields such as aerospace, defense, medical, and energy—amongst others—have taken advantage of these benefits, pushing material properties past what is attainable through conventional manufacturing. A wide variety of materials can be fabricated through AM, ranging from polymers, to ceramics, metallic materials, and composites. The focus of this work will be on the metallic systems.

Laser powder-bed-fusion (L-PBF) is a prominent metal AM technique that offers high spatial resolution and an unparalleled degree of geometrical design freedom. Components with intricate internal features, otherwise impossible to produce with subtractive manufacturing (e.g. computer numerical control (CNC)), can be designed and printed in a matter of hours [6]. The controlled environment of the process also enables location dependent control of material properties, by leveraging the numerous combinations of printing parameters and environments existent to date. From a design perspective, the efficiency of L-PBF can be used to rapid prototype components without having to invest in mass production devices, such as casting molds. Therefore, L-PBF is revolutionizing design timelines, versatility, and cost, without having to sacrifice precision or quality [7,8].

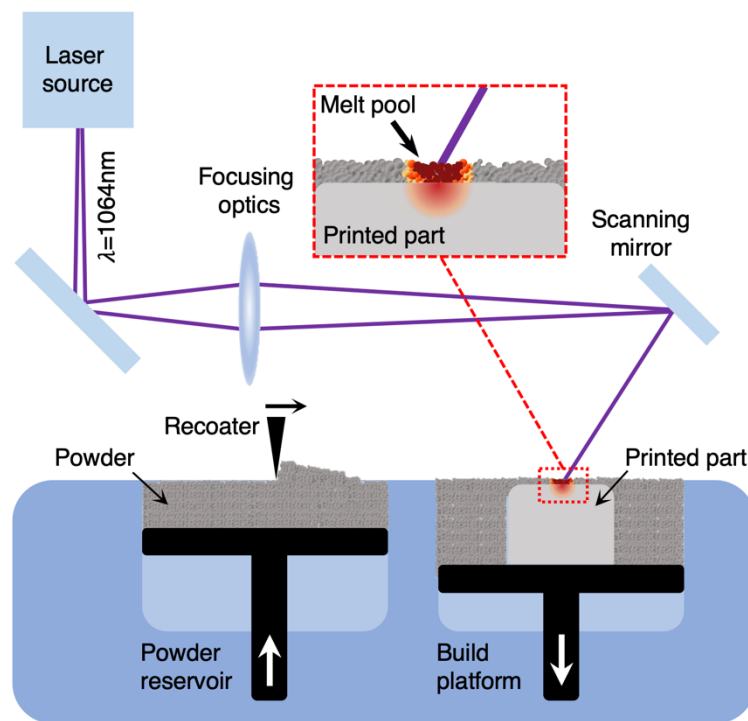


Figure 1 | Laser powder-bed-fusion (L-PBF) schematic. A high-power laser is focused through optics onto the powder-bed, locally melting the metal powder into the desired geometry. The insert shows the melting process of a layer onto the previous ones. The build plate is then lowered and a recoater lays a fresh layer of powder from the reservoir. The process is repeated iteratively until the desired component is obtained.

As shown schematically in Figure 1, L-PBF machines typically consist of a build plate, a powder reservoir, and a laser source. Optics are employed to focus the laser beam onto fine metal powder to melt the exposed layer into the needed geometry. The setup is encapsulated in a build chamber that can be purged with inert gases (e.g. argon, nitrogen) during printing, to minimize impurities and contamination [9]. L-PBF offers a variety of customizable options, such as heating stages that reduce the temperature gradients and cooling rates of the samples, vacuum chambers to near fully eliminate any airborne contamination, and multiple lasers and/or recoaters to minimize time between melting of subsequent layers. A variety of custom detectors can be attached to the printer to monitor production, improve its reliability and reproducibility, and custom tailor properties. Typical monitoring devices include high-speed and thermal cameras, to visualize local fluid dynamics and heat dissipation of the sample, as well as laser scanners to track the surface morphology of the printed layers. Thanks to recent developments in machine learning algorithms and computational power, live detection of the printing environment can be analyzed to optimize and predict properties by leveraging feedback loops.

The printing process begins with the creation of a three-dimensional file, typically computer aided design (CAD). Once generated, it is converted into a stack of 2D layers separated by a pre-defined layer thickness by using available 3D printing software. The new file, typically a stereolithography (STL) file, is then sent to the printer's control software. Printing begins when the recoater spreads powder from the reservoir to the build plate; the laser is then turned on and deflecting mirrors are used to raster the beam across the powder bed in the required geometry. Subsequently, the build plate lowers to allow more powder to be deposited, while the reservoir

raises to provide more powder to the recoater. The process is repeated iteratively, effectively welding each layer to the previous ones, until the desired component is obtained. Depending on the material, different laser wavelengths, sizes, powers, and scanning speeds, amongst other variables, can be selected. System specific parameters used in this work will be specified in each respective chapter.

1.3 Printability and properties of AM metals

While tens of thousands of metal alloys exist and are manufactured through conventional techniques (e.g. casting, molding, etc.), AM imposes limitations on their printability. The highly localized nature of the lasers exposes the metal powders to extreme environments. This technique generally results in drastic cooling rates and temperature gradients on the order of 10^6 - 10^7 K/m and 10^5 - 10^7 K/s, respectively. Severe, non-equilibrium conditions give rise to complex fluid dynamics, solidification behavior, and phase transitions-- all of which compete in timeframes that are infinitesimally small relative to conventional manufacturing processes [10]. Simultaneously, the iterative nature of L-PBF exposes the system to extreme thermal cycling, which can in turn promote formation of new phases, residual stresses, and heterogeneous microstructures—cracking often ensues as well during this stage, depending on the material chosen. These factors tend to create complex, hierarchical microstructures that can be engineered to obtain exceptional properties [11–16]. In general, L-PBF tends to refine microstructural features, resulting in higher strengths. Even though increased strength typically implies a reduction of ductility in metals, the freedom design inherent to AM often allows to bypass this trade-off, enabling improvement of strength alongside retention of ductility.

Typical signatures of AM metals include features such as unusual grain boundary distributions, tortuous grain shapes, chemical heterogeneity and segregation, high percentages of low-angle grain boundaries, and dense dislocation structures [11,14,17–24]. The ability to control multiple length scales of microstructure, referred to as hierarchical design, makes AM one of the most versatile techniques in metallurgy. Though microstructural engineering can theoretically offer millions of AM parameter combinations, and respective properties, many alloys suffer from printability issues, usually in the form of cracking. Two examples showcasing the solidification cracking effect in L-PBF will be investigated in the following sections and chapters.

1.3.1 High-strength aluminum alloys

High-strength aluminum alloys (2xxx, 7xxx series) are a class of materials that are employed in a variety of industries for which high specific strength ($\text{MPa}/\text{g}/\text{cm}^3$) is required [18,20,23,25]. Typical applications are found in the aerospace and automotive fields, where structural integrity and light weight are crucial [18]. The main strengthening mechanism responsible for these materials is precipitation hardening. Part of this work focuses on the 7xxx series alloys, which contain Al, Mg, Zn, and Cu. Many phases can be formed during processing of these alloys, as a function of cooling rates, chemistry, and choice of heat treatments. In the highest strength candidates, which are typically heat treated to induce age hardening, the major strengthening phase is made of Mg and Zn in atomic ratios that vary between 1-2 [26–37]. Due to the metastable nature of these precipitates (unless over aging is carried out, transitioning into a stable MgZn_2 phase), the literature is not in clear agreement on either the atomic ratios of said phases, nor their crystal parameters. A thorough understanding of the precipitation mechanisms in

L-PBF Al-Mg-Zn-Cu, and their impact on printability and mechanical properties, has not yet been adequately presented in the literature.

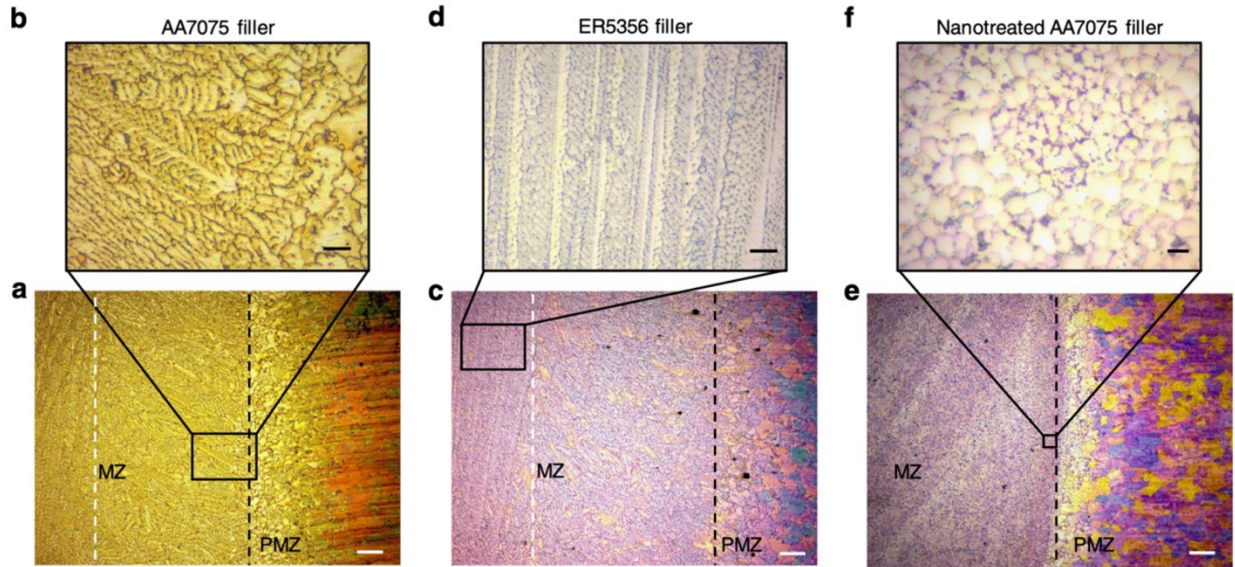


Figure 2 | Comparison of three different filler materials used in welding. The nano-treated 7075 filler yields a fine, equiaxed structure with no cracking, as opposed to the more columnar/dendritic microstructure in the first two samples. Scale bars are 200 μm in **a**, **c**, **e**, 50 μm in **b**, **d**, 10 μm in **f** [41].

Due to Mg and Zn having high vapor pressures and low boiling points (1090°C and 907°C boiling temperatures, respectively), the L-PBF process evaporates significant amounts of these solute atoms during printing [28,38,39]. To compensate for this effect, metal powders used in AM often have much higher concentrations of these metals. In addition to the atypical chemistry, L-PBF also creates the highest cooling rates in AM, generating microstructural and chemical landscapes that can be starkly different from conventional equivalents [3,17,28,40]. Unfortunately, these alloys can suffer from what is known as ‘hot tear cracking.’ This phenomenon is often encountered in welding, where these classes of high-strength Al alloys are colloquially labeled as “unweldable”; AM provides a similar environment during manufacturing due to its extreme localization of energy on a small surface, resulting in rapid cooling [18,20,27,28,38,41–47].

During solidification, the alloys' wide semi-solid zone activates local instabilities of solute concentration that result in the promotion of dendritic solidification. At high cooling rates, pockets of liquid are trapped between dendrites and, upon further cooling, differences in volume between solid dendrites and liquid pockets create large stresses that induce cracking along the solidification lines [20,41,47].

Successful crack mitigation strategies have been reported in recent years: inoculants such as TiC nanoparticles have been shown to slow the solidification front, while simultaneously providing heterogeneous nucleation sites that refine the microstructure and suppress dendritic formation [20,38,41,46,47]. A comparison from the literature showing a welding solidification structure of a typical AA7075 filler, and a nano-treated equivalent are shown in Figure 2 [41]. Notice how the microstructure in Figure 2f-e is refined and equiaxed, as opposed to Figure 2a-b, where dendritic formations are found [41]. The same microstructure changes are seen in AM, as will be discussed in later chapters. Inoculants with similar effects have also been reported in AM: mainly TiB₂ and Zirconium nanoparticles [25,41,43,45,48–50]. Interestingly, the resulting mechanical properties of the printed components have been shown to drastically exceed those of cast equivalents. A balance between solidification-cracking suppression and quenching induced precipitation of strengthening phases must be carefully achieved for a successful AM component.

In this work we report the successful printing of a 7xxx alloy, as well as its unparalleled mechanical properties, which surpass any AM or conventional material in this class, as well as conventionally manufactured Ti-6Al-4V, a standard for high specific strength structural materials.

1.3.2 Tungsten and tungsten alloys

Tungsten (W) and its alloys are used in applications ranging from fusion energy and plasma-facing components to defense applications in extreme environments [17,19,51,52]. W has the highest melting temperature (T_m) of all metals (3422°C), excellent thermal conductivity, and high density (19.27g/cm^3). Due to its high T_m , tungsten is an interesting candidate for L-PBF, which can focus enough energy onto the metal to melt it with ease. Conventional manufacturing methods, such as sintering, limit the geometrical complexity of the obtained components, thus making AM an appealing alternative for fast, spatially precise, and geometrically complex parts.

The same properties that appeal to tungsten-based applications, however, also hinder its successful printing. Unlike aluminum alloys, tungsten suffers from a high ductile to brittle transition temperature (DBTT), a limitation inherent to its body-center cubic (BCC) crystal structure [53–58]. The exact DBTT of tungsten is not well defined, especially given its strong dependence on impurities. Studies have shown that increments in oxygen concentration of as little as 50ppm can increase the DBTT by over 100°C ; these limitations are unfortunately exacerbated by L-PBF [19,59,60]. Due to the printing environment not being completely oxygen free, and the extremely high cooling rates experienced in the process, upon cooling to room temperature the system is forced to the limits of its plastic ability, often resulting in cracking. Oxygen segregation, especially at high angle grain boundaries (HAGBs), is known to be a main contributor to embrittlement [17,19,54,61–66]. Several attempts to suppress cracking have been reported, mostly involving strategies such as parameter optimization, build plate heating, alloying, or a combination [57,67–70]. Examples of typical microstructures in L-PBF W are shown in Figure 3 [71]. Cracks are observed along HAGBs and tend to form in the direction of cooling (build direction). Slight columnar grains are seen in b, typical of AM. The bottom section of Figure 3 shows an example

of crack mitigation attempts via alloying. Its grain refinement effect with progressively higher alloying concentrations of Ta is presented. While cracks were reduced in the study, complete suppression was not achieved [67]. To date the published literature has not reported successful printing of crack-free W via L-PBF. In this work we provide a framework for printing this system by addition of a small (0.3 wt.%) amount of boron. For the first time, we also report tensile properties for L-PBF W, an excellent indication of the structural integrity (absence of cracking) of the system. High temperature properties (800°C) are also reported and discussed.

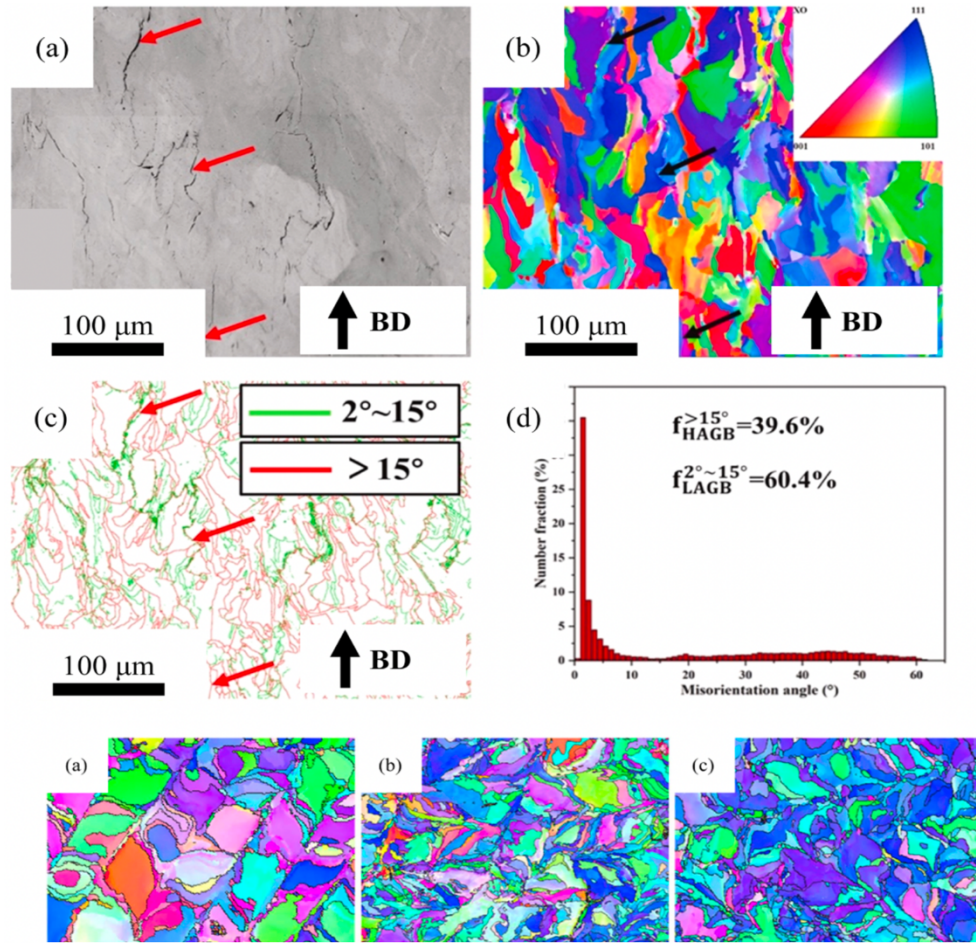


Figure 3 | Microstructural features in additively manufactured (AM) tungsten. Top: Electron Backscattered diffraction (EBSD) and scanning electron microscope (SEM) micrographs showing the formation of cracks predominantly on high angle grain boundaries (HAGBs) and along the build direction (BD). **Bottom:** EBSD maps of three Ta-alloyed L-PBF W samples. From

left to right, W-5 wt. %Ta, and W-10 wt.% are shown. Grains become more refined between **a**, **b**, while a smaller change is noticed in **c**. Cracks are not completely suppressed with this strategy, though they are reduced [71, 67].

1.4 Strengthening mechanisms in AM metals

AM metals tend to have complex, heterogeneous microstructures because of the extreme environments in which they are formed. These features often result in a variety of competing strengthening mechanisms that contribute to the materials' properties [11,12,14–16,72,73]. This work analyzes multiple systems, including single phase copper, a solid solution medium entropy alloy (CoCrNi), a 316L stainless steel, multiphase aluminum alloys, and a doped tungsten-based system. The material properties and intrinsic microstructural features of each system highlight different aspects of the effect of AM on metallic systems. A broad review of the main mechanisms is presented below.

1.4.1 Grain boundary strengthening

Grain boundaries (GBs) are defects that form when grains with different crystallographic orientations meet. At these locations high-energy areas with misfits and strains form; during plastic deformation, dislocation motion on close packed planes is hindered by GB's, which behave like obstacles [74]. As a result, dislocations can form pileups, which further prevent plastic motion and effectively strengthen the material. Because the mechanism is based on these 2D defects, an increase in boundaries density provides more strengthening, since dislocations have a higher chance of encountering a roadblock. Quantification of the resulting strengthening is described by the Hall-Petch relationship:

$$\Delta\sigma_{GB} = \frac{k_y}{\sqrt{D}} \quad (1)$$

where k_y is the Hall-Petch coefficient, describing the material-dependent strengthening effect, and D is the average grain size of the sample. It is evident that as grain size decreases, strengthening increases as a direct result of the higher GB concentration. This effect can be a significant contributor to the properties of AM materials-- especially in L-PBF, which tends to refine grain structures [74].

1.4.2 Solid solution strengthening (SS)

When solute atoms are introduced in an otherwise pure element matrix, the mismatch between atomic radii inevitably generates local strains and stresses. Depending on the size of the atom, both compressive and tensile stresses, as well as shear components, can form. Strain fields interact strongly with dislocations, thus contributing to strengthening by disrupting their motion [15,55,74–79]. Intuitively, the higher the concentration of solute or the misfit between atoms, the higher the effect, as shown by equation 2.

$$\Delta\sigma_{SS} = Gb\epsilon^{3/2} \sqrt{c} \quad (2)$$

In equation 2, G is the shear modulus of the matrix, b is the burger's vector, ϵ is related to lattice distortion and difference in moduli between elements, and c represents the concentration of solute atoms. Because AM metals tend to have heterogeneous microstructures, the effect of SS strengthening can be challenging to calculate. Often the above equation is used as an upper threshold of strengthenin— assuming the limiting case in which all solute atoms are well dispersed in the matrix without any precipitation or segregation.

1.4.3 Dislocation strengthening

Pre-existing dislocations in the matrix, like most other defects, can also hinder plastic flow. If the matrix already has a high concentration of dislocations before loading, entanglement takes place, effectively preventing dislocations from moving past each other [74]. This relationship between density and strengthening is described by the Taylor hardening equation:

$$\Delta\sigma_{disl} = \alpha MG\sqrt{\rho} \quad (3)$$

where α is a factor describing the dislocation arrangement, usually in the range 0.3-0.4, M is the Taylor factor (3.06 in untextured FCC systems), G is the shear modulus, and ρ is dislocation density. Dislocations can play a noticeable role in AM, since high cooling rates tends to ‘freeze’ the materials at rates high enough that dislocations must form to accommodate the large stresses and strains [12–14,73,80].

1.4.4 Precipitation strengthening

Precipitation refers to the tendency of solute atoms to form different phases relative to the matrix by rearranging elements into more energetically favorable positions; these obstacles then hinder plastic flow. High-strength aluminum alloys are an excellent example. The 7xxx series (Al-Mg-Zn-Cu) generate a variety of phases during manufacturing, of which the η/η' phases are the ones typically responsible for most of the strengthening. Precipitates can be either coherent, semi coherent, or incoherent with the matrix. Depending on the interaction between phases, their sizes and distribution, and chemical makeup, two main strengthening mechanisms can take place [29,34,81–86]. The first, typically found in smaller, coherent precipitates is shearing. Briefly, as dislocations glide through the matrix they impinge upon a coherent second phase. If the conditions are right, the dislocation will effectively cut through it, dividing the particle into two. The energy

associated with this motion strengthens the system [26,87]. Equations 4-7 outline the individual factors that play into the process. Briefly, the main contributors are volume fraction, size, lattice spacing misfit, and elastic properties of the shearable particles. A more detailed discussion will be presented in Chapter 3.

If the precipitate is semi or incoherent, dislocations can bypass it by bowing around it in what is known as Orowan looping. Notice how equation 4 does not depend on chemistry (G is the matrix modulus). This is because dislocations only see a non-coherent obstacle that needs to be circumnavigated—however, no actual interaction occurs with the inside of the particle, thus rendering its chemistry uninteresting [75,81].

Because these mechanisms are competing, two sets of equations must be compared to predict which mechanism will be active. To determine which equation applies, a strengthening map can be made by employing all equations 4-7 simultaneously and by defining that Orowan looping is active if $\Delta\sigma_{orowan} < \Delta\sigma_{cs} + \Delta\sigma_{ms}$. The variables used in equations 4-7 can be found in [81].

$$\Delta\sigma_{orowan} = M \frac{0.4Gb \ln\left(\frac{2\bar{r}}{b}\right)}{\pi\sqrt{1-\nu} \lambda_p}; \bar{r} = \sqrt{2/3}r \quad (4)$$

$$\Delta\sigma_{cs} = M\alpha_\epsilon (G\epsilon_c)^{\frac{3}{2}} \left(\frac{rf}{0.5Gb}\right)^{\frac{1}{2}} \quad (5)$$

$$\Delta\sigma_{ms} = M0.0055(\Delta G)^{\frac{3}{2}} \left(\frac{2f}{G}\right)^{\frac{1}{2}} \left(\frac{r}{b}\right)^{\frac{3m}{2}-1} \quad (6)$$

$$\Delta\sigma_{os} = M0.81 \frac{\gamma_{apb}}{2b} \left(\frac{3\pi f}{8}\right)^{\frac{1}{2}} \quad (7)$$

The resulting map (example shown in Figure 4) helps visualize the volume fraction and size of the precipitates that would be needed to obtain a specific degree of strengthening for an Al 7xxx alloy.

The white contour lines have units of strengthening (MPa).

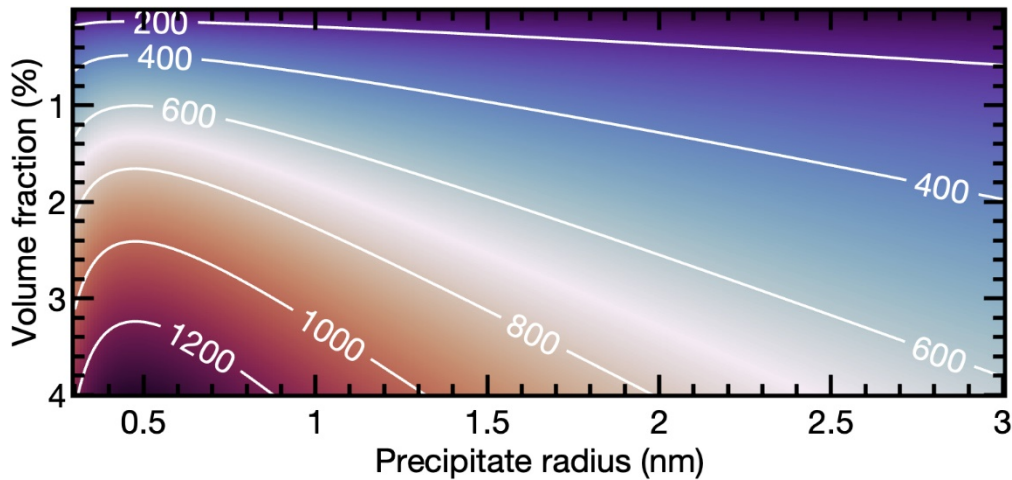


Figure 4 | Precipitation strengthening map of a Al7xxx series alloy. The map was generated by using equations 4-7 and parameters specified in Chapter 4. The white contour lines have units of MPa, representing the strengthening effect of the precipitates in the system for different combinations of phase fraction and precipitate size.

Plastic deformation of AM systems requires careful understanding of the interplay of all the strengthening pathways mentioned above. Advanced characterization techniques are used in this work to unravel these mechanisms, thus improving our understanding of the benefits and limitations of AM.

1.5 Characterization of AM metallic systems

The field of metallurgy has existed for millennia. In its early stages, understanding the properties of naturally found metals (such as copper) involved distinguishing properties like workability and sharpness (i.e. tool making) and visual attributes like color [1]. Deliberate

engineering of metals only came into play during the bronze ages, when it was discovered that small additions of other elements (i.e. alloying) changed the behavior of the material. Processing of metals through heat treatments and quenching treatments gained popularity only around the Roman Empire centuries: observations regarding steel quenching in water, as opposed to oil, were carefully considered to obtain a balance of hardness and ductility of metal weapons and tools [1,88,89].

While these discoveries paved the road for the centuries to come, deeper scientific understanding had to wait until the 18th and 19th century, at which point chemical analysis and the advent of optical microscopy lead to the first observations of microstructural features. Soon after, at the beginning of the 20th century, X-ray diffraction and electron microscopy became two of the most important metallurgical characterization techniques, allowing researchers to hypothesize and validate theories on the atomic composition, structure, and behavior of metallic systems. In the following 100 years exponential improvement of these techniques quickly accelerated the field of characterization; during the 1960's, generation of electromagnetic radiation through synchrotron facilities quickly gained popularity in the scientific world, enabling an unprecedented level of precision and insight into metallurgical behavior [90,91].

Today, metallurgists and material scientists routinely operate improved iterations of these technologies to image individual atomic positions and chemical composition through electron microscopy, and measure lattice spacing changes on the order of a fraction of an atomic length through synchrotron diffraction. While a variety of advanced techniques are utilized, the core of this work leverages synchrotron x-ray diffraction (SXRD) and high-resolution electron microscopy (EM) to understand the processing-structure-property relationship of AM materials.

We discuss various strengthening and plasticity mechanisms during in-situ mechanical loading via SXRD—simultaneously, we employ atomic-resolution EM to validate, and expand on, the results.

Even though over 2000 years separate us from Roman metallurgical practice, the fundamental goal of its applicability remains the same: leveraging empirical observations to understand and optimize the strength-ductility relationship of metallic systems, while suppressing catastrophic failure.

1.6 Research outline

This work sheds light on the printability of various L-PBF material systems and their resulting mechanical properties. In-situ experiments, alongside high-resolution EM imaging, are used to investigate the deformation mechanisms in multiple metallic systems, paving the road for a deeper understanding of plastic behavior of L-PBF metals. The structure of the dissertation is as follows:

- **Chapter 1** provides an overview of additive manufacturing of metallic systems via L-PBF. Printability limitations of the technique are discussed for two systems, a boron-doped tungsten material, and a high-strength aluminum alloy. Active strengthening mechanisms are presented in relation to their role in AM metals. A brief history of metallurgy and the evolution of characterization techniques is explored.
- **Chapter 2** outlines the specific methodologies used throughout the work. Emphasis is given to SXRD, used to probe deformation of multiple FCC systems in real time. EM is also discussed in detail, as it is used as a complement to SXRD in the following chapters.
- **Chapter 3** expands on the printability issues of W systems in L-PBF. A framework for its successful printing is provided. A combination of XRD and HR-TEM are presented to understand

the relevant crack suppression mechanisms, and to explain the excellent strength and ductility of the system at 800°C.

- **Chapter 4** investigates a 7xxx series aluminum alloy, explaining the benefits of nanoparticle inoculation to suppress hot tear cracking during AM. A variety of characterization techniques (SXRD, SEM, EBSD, TEM...) is then used to shed light on the deformation mechanisms responsible for the material's excellent mechanical properties, which surpass any equivalents in the literature.
- **Chapter 5** delves deeper into the use of in-situ SXRD analyses by comparing four independent FCC systems. Different deformation mechanisms are highlighted for each, providing a framework to use SXRD in AM material optimization.
- **Chapter 6** briefly discusses the applicability of this work to other systems, highlighting possible research directions for future work.

Chapter 2. Experimental methods

2.1 Introduction

This chapter discusses the methodology that is central to this work, namely Synchrotron X-ray Diffraction (SXRD) and electron microscopy (EM). An introduction to the basic working principles of synchrotron radiation and its applicability to the analysis of deformation mechanisms in AM systems is presented. Signal generation in EM is also explained, and related characterization techniques used in this work are introduced (e.g. electron backscattered diffraction (EBSD), secondary and backscattered electrons (SE/BSE), energy dispersive x-ray spectroscopy (EDS/EDX), and transmission/scanning electron microscopy (TEM/SEM)). Specific experimental parameters used in chapters 3-5 can be found in the respective experimental sections.

2.2 Synchrotron X-ray diffraction for mechanical properties

2.2.1 Working principles of X-ray diffraction

X-ray diffraction (XRD) is a widely used, non-destructive technique that gives insight into the crystal structure of materials [91,92]. Interpretation of XRD spectra relies on Bragg's law, which geometrically relates the orientation of crystalline atomic planes in the sample to the incoming x-ray beam according to equation 8.

$$2d^{hkl} \sin(\theta^{hkl}) = \lambda n \quad (8)$$

Here, d^{hkl} is interplanar spacing, θ^{hkl} is the angle between the atomic planes and the incoming x-ray beam, λ is the wavelength, and n is an integer representing diffraction order (Figure 5b, top). The subscripts 'hkl' specify the miller indices of respective atomic plane orientations (e.g. {111}),

$\{100\}$, $\{110\}$). Typical planes of interest in cubic systems are schematically shown in the cubic unit cell in Figure 5c.

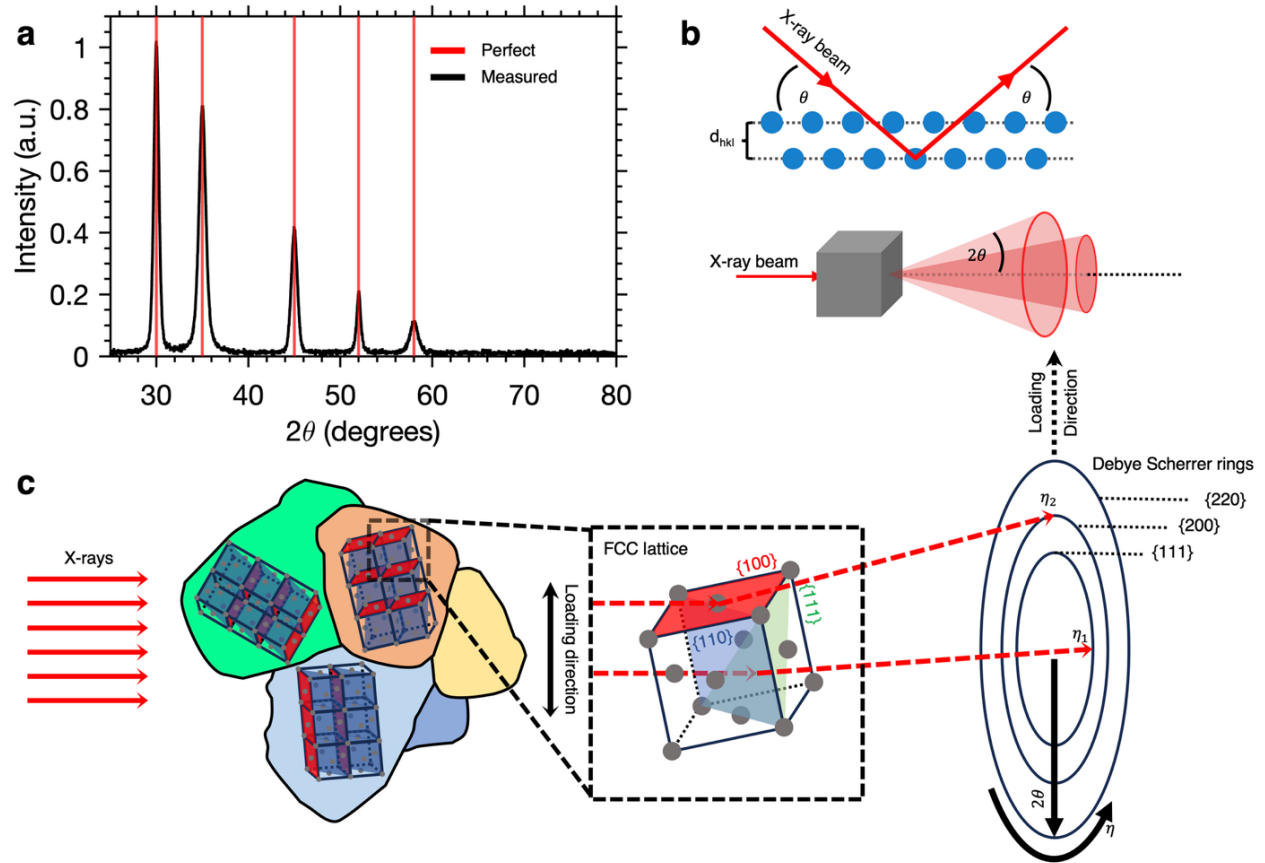


Figure 5 | Schematic of x-ray diffraction. **a** Example of x-ray diffraction (XRD) spectra. The red lines represent the theoretical positions that satisfy Bragg's law. Measured data points in black show a distribution of intensities around the theoretical values. **b** Schematic showing the geometry of Bragg's law. Blue dots represent atoms lying on rows separated by interplanar distance d_{hkl} . Theta is the angle between the plane and the incoming beam. The 3D equivalent showing diffraction cones emanating from a polycrystalline sample is shown below it. **c** X-rays penetrate the sample (transmission geometry), they then interact through scattering with groups of unit cells with different orientations (grains). Depending on where Bragg's law is satisfied, Debye Scherrer rings can be collected on a 2D detector. Rings form because of the random orientation of grain orientations, like in powder diffraction. While patterns are collected, tensile testing can be performed, as indicated by the loading direction (black, dotted arrow).

As X-rays interact with matter, constructive and destructive interference from electron scattering results in distinct intensity patterns that carry physical information about the system. Figure 5a shows a typical spectrum (Intensity vs. 2θ) for a crystalline material. The angular locations where peaks appear correspond to those that satisfy Equation 8. Notice that Figure 5a shows multiple peaks—implying that the analyzed sample is polycrystalline and has at least four distinct grains oriented in such a way that they independently satisfy Eqn. 8. The bottom schematic in 5b is a 3D equivalent to the one above it, showing that diffraction conditions can be satisfied according to Bragg's law along the surface of the red cones. If a 2D detector is available and placed behind the sample being irradiated, the projections of the cones onto the flat detector generate Debye-Scherrer rings. Each ring represents signal intensity of specific grain orientations (Figure 5c).

One of the major drawbacks of laboratory XRD set-ups, however, is the shallow penetration depth of x-rays. This limitation is mainly due to the x-ray source, usually produced by bombardment of a known target material with accelerated electrons (Figure 6a). Electron collisions can excite an electron into a higher orbital; when it returns to its original lower energy state, x-rays with energy equal to the orbital energy difference are released (e.g. Cu K-alpha1, Cu K-beta2 etc.) [91,92]. Unfortunately, most elements have multiple electron orbitals, which cause emission of more than one wavelength at a time. Issues quickly arise due to interference of overlapping signals, which either need to be considered during peak analysis, or need to be filtered out at the expense of signal intensity. Loss of intensity further complicates achieving a strong enough signal to obtain information that is representative of the bulk microstructure. Solving this issue requires X-ray sources with higher energies and brilliances.

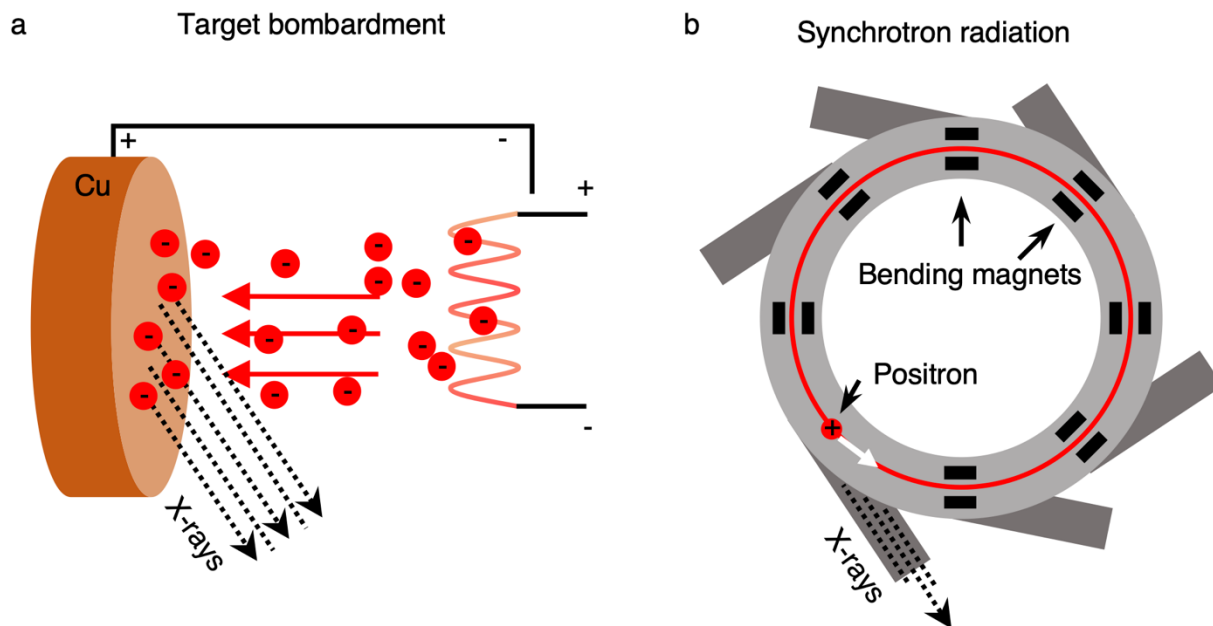


Figure 6 | Generation of X-ray signal schematic. **a** A copper target is bombarded with accelerated electrons from an emission source. As electrons collide, Cu electrons are excited into higher orbitals, subsequently releasing energy in the form of x-rays. The wavelength is tied to the orbital energies of the element. **b** Bird's eye view of a synchrotron facility. Charged particles are accelerated centripetally via strong bending magnets. As relativistic speeds are approached, high energy x-rays are released tangential to the path of the particle. The energy is a function of the speed of the particle, allowing tunability in energy, high monochromaticity, and high brilliance.

Target bombardment (Figure 6a) is not the only way to generate X-rays. Physical laws tell us that electromagnetic waves are produced when electrons (or charged particles) are accelerated. By adopting a centripetal acceleration geometry in infrastructures that allow for particles to travel at relativistic speeds, x-rays of much higher energy and brilliance can be produced, as shown in Figure 6b. Bending magnets are used to constantly accelerate particles around the synchrotron ring; centripetal acceleration causes x-rays to be emitted tangential to the path of the particle, ready

to be used for sample measurements. This is the working principle on which Synchrotron accelerators operate [90,93].

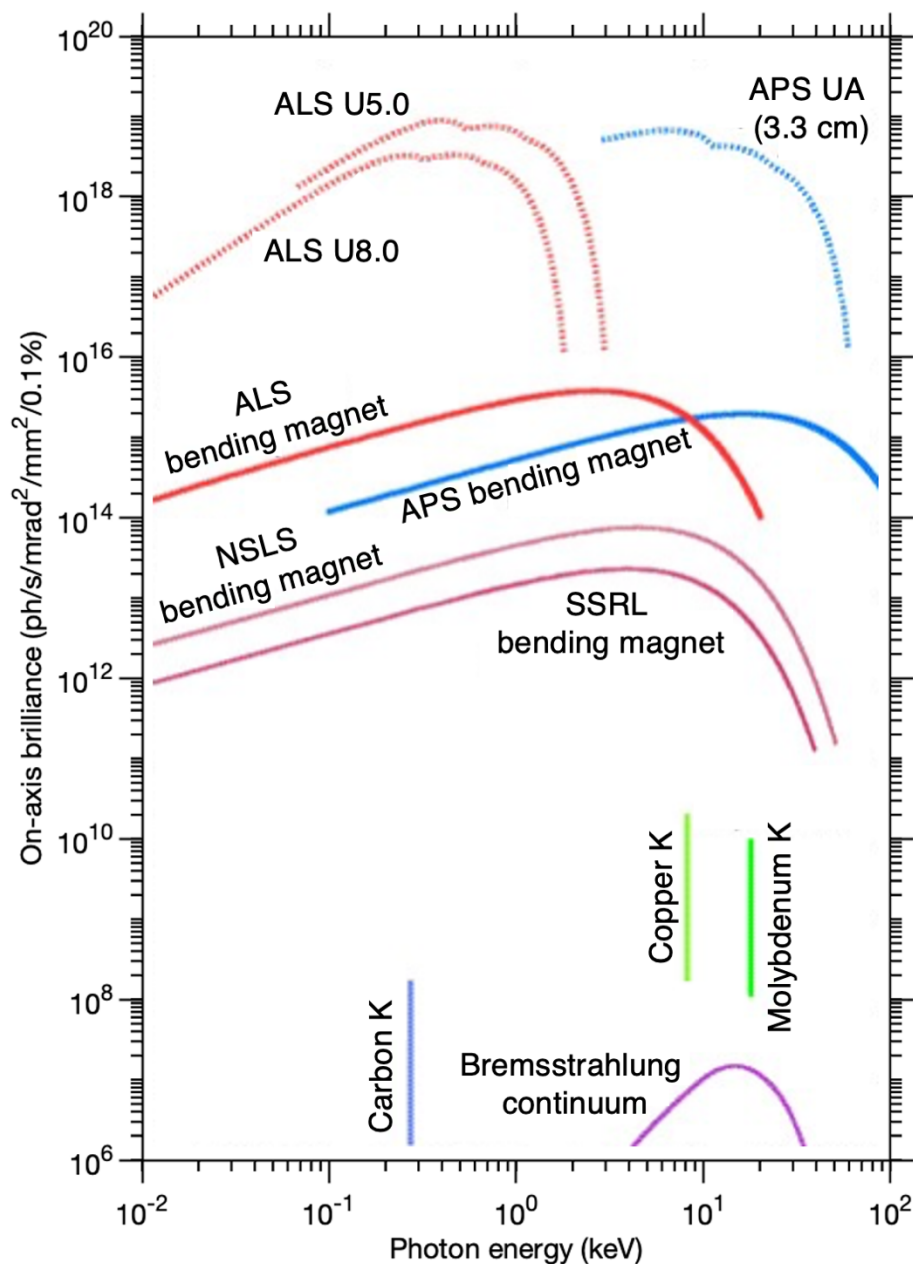


Figure 7 | X-ray brilliance comparison. Typical laboratory metal targets (Copper K, Molybdenum K) and latest generation synchrotron brilliances sources are compared. The difference can be as high as 10 orders of magnitude.

High energy synchrotron sources can create x-rays with energies above 100keV, as opposed to target bombardment energies, which are on the order of 8-17keV (e.g. Cu-K, Mo-K). Even more importantly, synchrotrons are capable of generating brilliances that are close to 10 orders of magnitude higher than those generated by any metal target (Figure 7). The issue of signal reduction due to penetration depth is thus virtually eliminated, allowing for x-ray transmission through samples that can be millimeters thick (depending on beam energy and element Z number). Sampling from much larger volumes is then possible, enabling statistically significant measurements that describe bulk behavior, rather than just surface information. Highly calibrated focusing optics allow to obtain x-ray signals with excellent monochromaticity, which is leveraged to obtain extremely precise measurements, without issues arising from overlapping orbital signals.

In a theoretically perfect system, Bragg angles are exact orientations at which constructive interference, and therefore a detectable signal, arise. In practice, these angles are rarely exact and are instead shifted and/or spread over a range of values (Figure 5a). This deviation from ideal behavior is used to infer physical attributes of the system and analyze its behavior under external stresses. Many materials have well-defined XRD spectra that have been meticulously characterized over the past century, allowing identification of many materials. XRD databases can be used to perform analyses of internal strains and stresses, texture evolution, phase transformations, as well as defect evolution through a combination of peak shift analysis and line profile analysis (LPA) [94]. The next sections will expand on these techniques.

Another key strength of SXRD lies in the ability to probe material behavior in real time. Various set-ups exist around the world that enable in-situ monitoring of material deformation under stimuli such as stresses and strains, temperature, pressure, impact etc.; in this work we focus

on in-situ tensile loading [11,21,73,95–104]. Here, a dogbone sample is loaded onto a mechanical testing machine in any combination of tension, compression, or torsion, while x-rays are continuously transmitting through it. Live diffraction patterns are then collected on a 2D detector placed behind the sample (Figure 5c). Provided that the specimen is fine grained, circular patterns known as Debye-Scherrer rings arise from the stochastic orientation of thousands to millions of grains in the sample as they diffract according to Bragg's law. The tendency of L-PBF to refine grain size—thus increasing number of grains per fixed volume-- allows to fully take advantage of SXRD technology. Average bulk measurements are particularly important for the study of AM materials because their microstructures can be highly heterogeneous. If signal is only collected from a small fraction, or surface of the samples, the chances of the signal being representative of bulk behavior are low.

2.2.2 *Pattern calibration*

Before any data processing is carried out, the diffraction ring patterns need to be calibrated. Standard procedures use known references such as LaB_6 or CeO_2 powders to collect a diffraction pattern at the same location at which the sample will be placed. Because the standard is well known, fitting its ring shapes describes the exact orientation of the detector. These parameters include Z (distance between detector and sample) and two rotation angles, which account for any tilt of the detector relative to the incoming beam. Once those parameters are obtained, a calibration file can be created and subsequently applied to all following patterns to ensure accurate measurements, so long as the geometry of the measurement is not altered.

The focusing optics used at beamlines are very well calibrated; however, some instrumental broadening still exists (e.g. beam divergence, beam shape). As a result, the standard reference

patterns need to be integrated to obtain a reference peak profile spectrum. By carefully fitting the reference peak shapes as a function of 2θ , it is then possible to extract an instrumental parameter file that defines the contribution to intensity peak shape of the focusing optics, rather than that of the sample being tested. All samples in this work were calibrated using a CeO_2 reference.

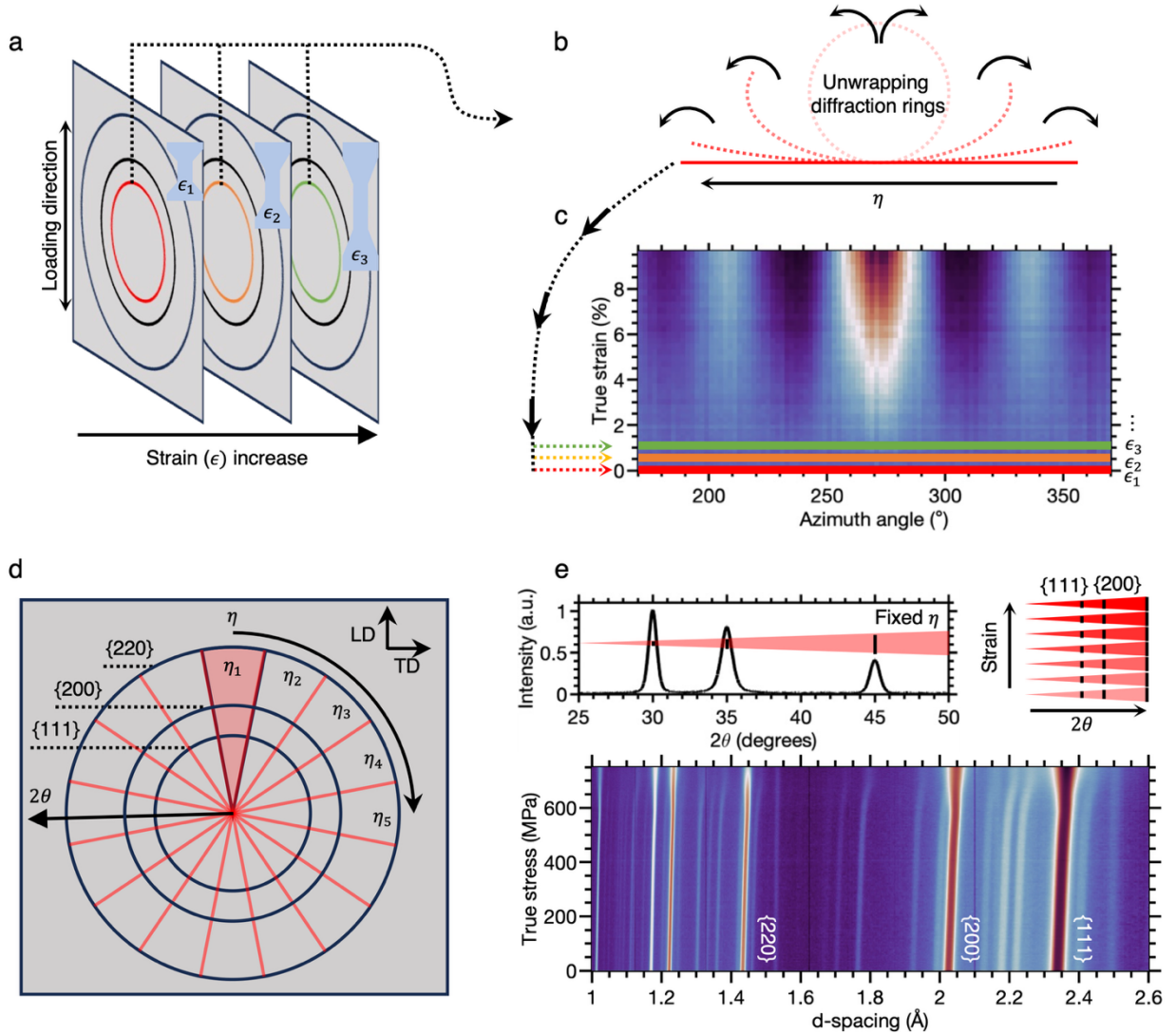


Figure 8 | Synchrotron data processing. **a** Schematic of Debye Scherrer rings collected from in-situ synchrotron. Multiple patterns are collected during loading. **b** A ring of interest ($\{111\}$ in this example) is chosen and its relationship to azimuth is converted from polar to cartesian, effectively “unwrapping” the ring. **c** The process in **b** is repeated for every strain level, generating multiple unwrapped rings representing intensity. The data is then stacked (colored lines) and an image showing the texture evolution during loading as a function of strain and azimuth is created. **d** Schematic of azimuthal slices used to divide the diffraction rings. **e** Each slice in **d** represents an

intensity plot at a specific azimuth location. Stacking these slices form different strain/stress levels during loading leads to the plot displayed on the bottom right.

2.2.3 *Data processing*

The analysis of diffraction peaks and its subsequent processing have become exceptionally fast with the advent of new generation synchrotrons and more efficient computing power. Collection of a single 2D ring pattern (encompassing 360 degrees of information, Figure 8d), only requires a fraction of a second, whereas the equivalent measurement would take hours of continuous data collection in a typical laboratory XRD set-up. Collection speed is of key importance during a quasi-static tensile test, where data need to be acquired every few seconds to accurately observe the activation and unfolding of atomic scale deformation. As a result, hundreds of patterns lead to large amounts of data, with a typical in-situ tensile test requiring tens of gigabytes of raw data. Sequential processing of diffraction data through optimized software such as GSAS-II and MAUD allows for the generation of results in a timely fashion.

Data structuring is also a key component of this work. Figure 8 shows the steps taken to generate two of the more complex plots presented in Chapter 4 and 5, for the sake of clarity. Figure 8a shows a schematic of multiple diffraction ring patterns collected at different strain levels during a tensile test—a more detailed representation of one of those patterns is displayed in Figure 8d, where the 2θ and azimuth (η) angles are defined. The first plot that will be discussed is a texture evolution plot (i.e. tracking how grains with specific orientations reorient themselves during plastic flow induced by tensile loading).

First, a reflection of interest is chosen, such as $\{111\}$ (colored inner circles in Figure 8a). By transforming the signal from polar (a ring) to cartesian coordinates (a line), the ring can be effectively ‘unwrapped’, as shown in Figure 8b. These lines represent peak intensity variation around the rings. The process is then repeated for all stress/strain levels, and the resulting lines are subsequently stacked in a matrix as shown in Figure 8c. The concept of ‘unwrapping’ is presented for ease of understanding; the full procedure used in this work is as follows:

1. Each image containing multiple diffraction rings is first subdivided into azimuth ‘slices’ as shown in Figure 9d.
2. Each slice is then integrated along its width to obtain an Intensity vs 2θ plot (Figure 8e) for all η 's.
3. The reflection of interest from each slice is then isolated (e.g. $\{111\}$ peak) and its area is integrated to obtain its cumulative intensity.
4. The process is repeated for all strain/stress levels, and the resulting intensities vs azimuth angle are stacked on top of each other to generate plots like in Figure 8c. This is equivalent to the ‘unwrapping’ technique.

Intuitively, the plot visualizes how grains with specific orientations (i.e. $\{111\}$) reorient themselves in different directions around the rings as the sample is deformed. While intensity is shown in the figure, other variables can be plotted as well (i.e. lattice spacing, lattice strain, or peak widths can be fitted and plotted instead of cumulative intensity).

The second example in Figure 8e uses a similar approach. The fixed variable in this case is no longer reflection family (a ring), but diffraction direction (azimuth location). Once an η is

chosen for all strain/stress levels (e.g. the red shaded area in Figure 8d), each slice is integrated and results in a vector representing peak intensity for all reflections (Figure 8e). Once again, stacking these vectors as a function of strain/stress results in plots like Figure 8e, showing the evolution of all 2θ angles (related to atomic spacings by equation 8) along a specific azimuth during tensile loading. Chapters 4 and 5 expand on the trends of these plots and their relation to deformation mechanisms.

2.2.4 Peak Shift Analysis

As implied by the Debye-Scherrer rings in Figure 8d, multiple diffraction families can be simultaneously tracked in polycrystalline samples. The ability to monitor their change as a function of macroscopic stress/strain offers insight into the atomic scale mechanics unfolding in the sample with extreme precision. When crystal structure parameters for the system of interest are known, it is possible to quantify relative peak shifts. Akin to a regular stress-strain test, in which macroscopic stress and strain are plotted, in-situ SXRD allows us to record the elastic (as opposed to plastic) response of individual $\{hkl\}$ planes. Plots of atomic lattice strain as a function of applied stress then yield the microscopic equivalent of a macroscopic stress-strain curve. Lattice strain is calculated by converting Bragg angles to d-spacings by means of Bragg's law (Eqn. 8) and according to equation 9,

$$\epsilon_{hkl} = \frac{d^{hkl} - d_0^{hkl}}{d_0^{hkl}} \quad (9)$$

where d is the hkl interplanar spacing, and d_0 is either the reference spacing or the initial value.

Three lattice strain curves are shown in Figure 9, representing the first three FCC reflections of an AM Cu sample. Different crystallographic orientations, in anisotropic materials,

have different stiffnesses; therefore, a difference in slope between individual sets of reflections is expected. The most obvious difference is typically between $\{111\}$ and $\{200\}$, which are the stiffest and least stiff, respectively, in FCC systems [11,73,97,98,100,105–107]. Monitoring of elastic lattice strain as a function of applied macroscopic stress enables to directly measure the apparent hkl-dependent elastic moduli (stiffness) of materials. The slopes in the early stages of deformation (dotted lines in Figure 9) can be used to calculate elastic constants. A few values of measured E_{hkl} values are tabulated in Table 1.

Table 1 | Measured $\{hkl\}$ dependent Young's Moduli (GPa) for four 3D printed systems.

	$\{111\}$	$\{200\}$	$\{220\}$	$\{311\}$	$\{222\}$	$\{400\}$	$\{331\}$	$\{420\}$	$\{422\}$
Al (H6)	73.85	68.05	72.37	70.3	75.6	71.6	73.3	72.9	75.1
Al (HIP)	79.3	75.7	80.3	78.2	83.2	76.3	82	80.1	82.5
Al (AP)	79.5	76.2	78.9	78.6	82.1	77.6	79.67	78.7	80.4
Cu	156.4	109.3	145.8	129.5	163.8	109.3	151.7	133.9	151.6
316L	245.6	149.9	209.3	187.5	247.6	149.2	238.6	200.2	236.9
CoCrNi	282.5	157.9	253	202.1	279.7	150.4	284.6	219.2	244.8

2.2.5 Lattice strain deviation

Of note is the concept of lattice strain deviation, a simple method to track atypical elastic responses of a material. For measured 2θ angles, know wavelength, and lattice parameter (a), lattice strain deviation (l.s.d.) is calculated according to the equation 10:

$$l.s.d. = \epsilon_{hkl} - \frac{\sigma^{applied}}{E_{hkl}} \quad (10)$$

Here strain is the same as defined Eqn. 8, E_{hkl} refers to the hkl specific elastic modulus, and $\sigma^{applied}$ is the macroscopic true stress during loading [73,98].

Alongside tracking the initial elastic strain behavior of hkl reflections, the transition into the plastic regime (permanent deformation) offers insight into the microscopic response of the system. The term deviation refers to the departure from the ideal (purely elastic) response of metallic systems near and past yielding. Though macroscopic yielding is typically defined by the 0.2% offset rule, this approach represents an average of multiple grains and directions with different orientations [73,97,107–111]. Like what is shown in Figure 9, where not all hkl planes have equal elastic constants (slopes), their lattice strain deviation is also hkl dependent (Figure 9b).

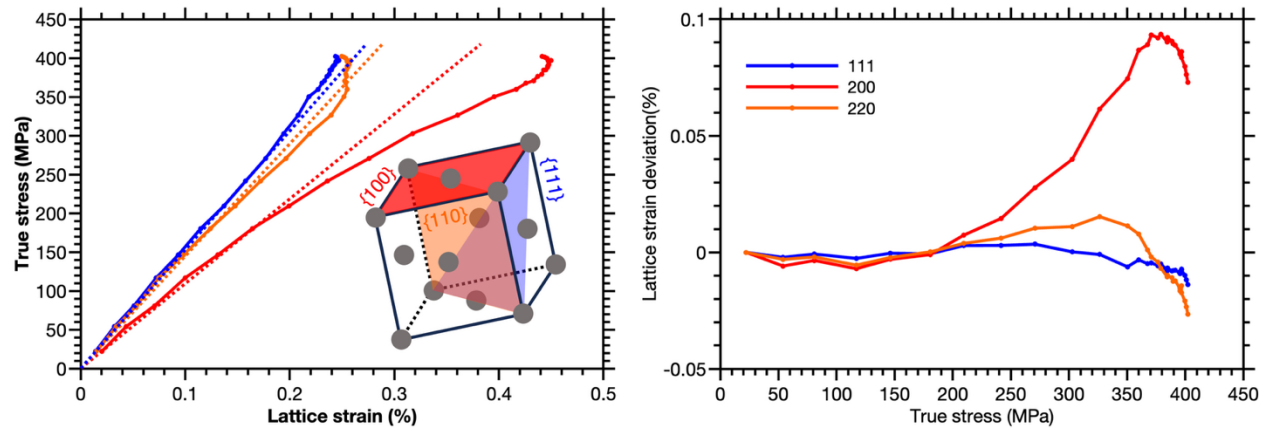


Figure 9 | Lattice strain and its deviation in additively manufactured Cu. Left: The initial elastic slope of the three curves is shown by the colored dotted lines. Notice how softer directions like $\{200\}$ have a much lower slope relative to the stiffest $\{111\}$ directions. An FCC unit cell is displayed for visual aid; colors are coded according to the legend. **Right:** Lattice strain deviation plotted according to equations (9) and (10). As typically reported in FCC systems, $\{200\}$ has the earliest and largest deviation from its ideal elastic behavior. The macroscopic yield strength of the material is around 300 MPa, far higher than the initial deviation point (~ 200 MPa). Opposite trends ($\{220\}$ going negative) imply plastic activity post-yield.

SXRD allows to directly measure the orientation dependence of yielding during loading, separating the contribution from different reflections. Figure 9 shows the strain deviation for an

AM Cu sample with softer and stiffer families of planes showing noticeably different lattice strain deviation behavior. Stiff, close packed planes (i.e. $\{111\}$) are the primary location of plastic flow in FCC systems; thus, their deviation from elasticity is expected to occur last, since softer reflections need to first exhaust their ability to elastically accommodate strain before plastic flow begins. On the other hand, softer planes like $\{200\}$ typically deviate sooner and with larger values [11,73,98]. Elastic lattice strain deviation trends can be used to infer the presence, prominence, and activation of various deformation mechanisms. This effect will be discussed in Chapters 4 and 5.

The above discussion omits a key piece of information: the orientation of the analyzed lattice strain relative to the loading direction. This information is crucial due to the Poisson effect, which relates the strain applied to a material in a specific direction (e.g. loading direction) to the resulting strain in the perpendicular direction [105]. The ratio of those strains is known as Poisson ratio (ν), defined as:

$$\nu = \frac{-\epsilon_t}{\epsilon_l} \quad (11)$$

where ϵ represents lattice strain, with subscripts t and l representing transverse and longitudinal directions. The negative sign indicates a contraction in the direction perpendicular to that of positive strain.

Similarly, on the atomic scale, elastic lattice strain and lattice strain deviation tend to have opposite trends when analyzed along LD, as opposed to the transverse direction (TD), because of the Poisson effect. Observing lattice strain behavior over the full azimuth (η) range, shown in Figure 8d, allows to precisely probe the elastic behavior of the material in 3D space [110].

2.2.6 Load partitioning

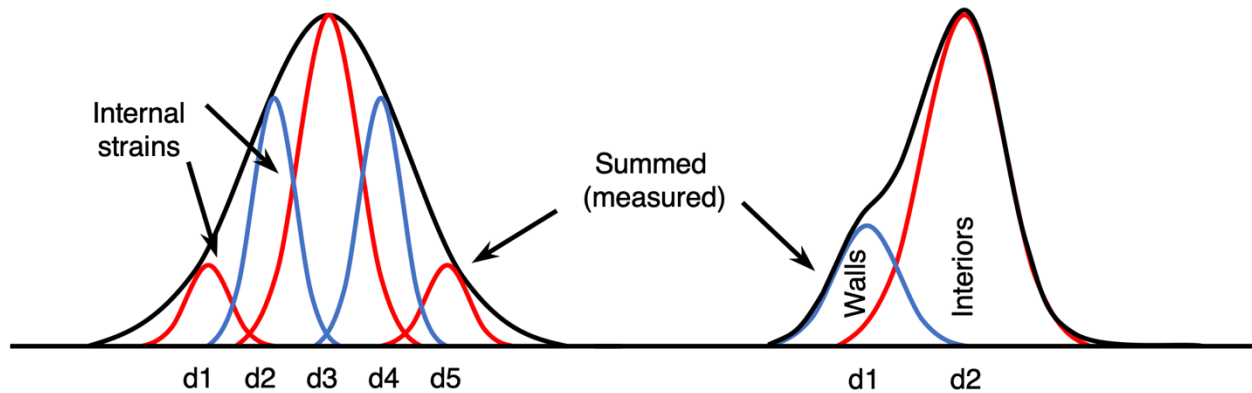


Figure 10 | Inhomogeneous strain broadening. a Inhomogeneous strains in a material create multiple peaks, centered around the unstrained, ideal peak position, due to slight differences in atomic spacing. The resulting peak therefore appears broader. **b** Similarly, features within the microstructure, such as chemical segregation or dense dislocation cells, create areas of different lattice spacings. Their sum can be perceived as asymmetric peaks.

In the case of a dual, or multi-phase material, reflections from different crystal structures can be tracked at once. As will be discussed in the following chapters, simultaneous tracking of different phases allows to understand the load-bearing interplay between matrix and intermetallics/precipitates, thus shedding light on the strengthening contribution of individual phases to the macroscopic properties [11,73,111–117]. By monitoring the relative behavior of these reflections' orientation relationships, their role in deformation can be studied in detail. Chapter 4 expands on this concept.

2.2.7 Line profile analysis

XRD peak position shifts reveal a myriad of details regarding the elastic/plastic behavior of metallic systems [94,118–127]. However, obtaining a well-rounded description of the

deformation processes involved requires the isolation of specific mechanisms. The field of line profile analysis (LPA) focuses on relating the shape (profile) of XRD peaks to structural defects within the sample. At a high level, Bragg's law states that only a set of very precise directions result in detectable signal. In this scenario, XRD spectra would be made of infinitesimally thin lines, rather than a distribution of intensities, as seen in practice (Figure 5a). This deviation from the Bragg condition is attributed to different kinds of structural defects. Broadly, peak broadening is generally synonymous to defect evolution and accumulation. Specifically, there are two main categories of broadening: strain and particle [91,92,94].

Lattice strains increase the width of peaks when local distortions change the interplanar spacing of atoms heterogeneously. If a gradient of strain is present, the width of the peak can be described as the sum of many smaller 'sub-peaks', each satisfying Bragg conditions, but with slightly different atomic spacings. Figure 10a shows a schematic of this process. Heterogeneous strains are visualized as different peaks with positions d1-d5, colored in blue and red. Because all peaks are only slightly offset from the 'ideal' unstrained position of the peak, the signal recorded by XRD appears as a broader, summed peak (black line). A similar scenario occurs when substructures exist within metal grains, such as dense dislocation cells or chemical heterogeneity. Strains in those regions can be different between cell interiors and walls, resulting in asymmetric peaks, as shown in Figure 10b [124,125,127,128].

On the other hand, particle broadening has to do with the size of scattering domains, which are regions of uninterrupted crystallinity within a sample (though not necessarily the same as grains). Relatively large domains (typically larger than 0.1-1 μm), can effectively be considered infinite, meaning that the diffracting signal resulting from x-rays penetrates through enough atomic

layers such that any incoherent scattering is compensated by deeper layers, rendering the effect negligible. As domain size is reduced, fewer planes with consistent orientation are present, occasionally preventing the compensation process. The resulting signal is therefore spread over a larger angular range, broadening the peak shape [94,120,122,123,127,129–132].

Strain and domain size can be considered independent of each other, which allows for decoupling of their respective contributions by adopting specific fitting procedures. Combinations of these types of broadening occur because of a variety of defects. For instance, dislocations, faults, twinning, and back-stresses can disrupt the periodicity of the lattice and create local strain fields, thus affecting the path of the x-ray signal and causing broadening. A more detailed discussion is presented in the later chapters. We note that line profile analysis assumes a texture free sample; this assumption needs to be carefully addressed before drawing conclusions, especially for L-PBF materials, where strong texture can form along the build direction [94].

SXRD offers a deep level of structural insight into deformed samples. In this work we leverage measurements from different systems (Al 7xxx alloys, Cu, SS316L, and CoCrNi) during tensile deformation to deepen our knowledge of elastic and plastic behavior in AM FCC systems. By comparing materials that possess independent deformation signatures (a pure copper system, a low stacking fault energy (SFE) solid solution alloy, a 316L steel, and a high SFE, multiphase alloy), we provide a robust reference framework for future investigation of other AM FCC systems.

2.3 Electron Microscopy

Electron microscopy (EM) served as a cornerstone technique for microstructural characterization across all metal and alloy systems examined in this work. Its value lies not only

in exceptional spatial resolution, but in the breadth of signals it can generate-- enabling insight into morphology, crystallography, and local chemistry. Fundamentally, EM relies on the interaction of a focused, high-energy electron beam—typically in the range of 5 to 300 keV—with solid matter. As electrons are accelerated toward a specimen and impinge on it, they undergo both elastic and inelastic scattering, producing a range of signals including secondary electrons (SE), backscattered electrons (BSE), transmitted electrons, and characteristic x-rays. Each signal carries distinct physical information [92,133]:

1. SE imaging relies on detection of inelastically scattered electrons, on the order of $<50\text{eV}$. Because of their low energy, SEs are easily collected on a nearby ETD detector, on which a positive voltage is applied to facilitate the process. As a result, SE imaging is sensitive to surface topology. Inelastically scattered electrons can also be used to obtain crystallographic orientation and phase information through electron backscattered diffraction (EBSD).
2. BSEs are on the opposite end of the energy spectrum, retaining almost all their energy after interaction with the sample. This behavior can be inferred by the location of BSE detectors, which are usually placed around the electron source, since almost inelastic scattering implies that electrons will be scattered at a 180-degree angle, backtracking along their original direction of motion. The extent of the deviation from the zero-loss, 180-degree scenario is heavily dependent on atomic number (Z), with higher Z numbers scattering more strongly, thus generating more signal. BSE detection is used to visualize different phases and elements in SEM, however without providing quantitative elemental composition.

3. As discussed in the previous section, electron bombardment on metals generates characteristic x-rays whose energy is exactly defined by the orbital transition energies of each element. During electron imaging, these x-rays can be detected with an energy dispersive x-ray spectrometer (EDS/EDX) and plotted as a signal versus energy map. Since each element has characteristic energies, quantitative chemical mapping is possible.

In this work, SEM was used extensively to examine surface morphologies, solidification structures, texture, and secondary phases. Secondary electron imaging allowed for high-resolution topographical mapping of as-printed surfaces, fracture surfaces, and melt pool boundaries. Backscattered electron imaging, owing to its sensitivity to atomic number contrast, was particularly useful in distinguishing compositional domains in multiphase regions such as tungsten and boride precipitates, and Mg-, Zn-, and Cu-rich segregated zones in aluminum alloys.

Electron backscatter diffraction (EBSD) was employed to assess grain orientations, crystallographic texture, and local misorientation gradients in both as built and heat-treated samples. EBSD operates on the principle of diffraction from inelastically scattered electrons. As electrons enter the sample and lose energy, they scatter in all directions. To maximize signal intensity and spatial resolution, the specimen is typically tilted to approximately 70° . Statistically, some of the electrons will scatter at angles that satisfy Bragg conditions, resulting in the generation of diffraction cones (like in XRD, Figure 5b). Because the signals are recorded on a phosphor-coupled detector placed just a few millimeters from the sample surface, only a section of the cones is detected, appearing as parallel lines, or Kikuchi bands (Figure 11a). The diffraction geometry, combined with known symmetry constraints, enables indexing of the bands' relative positions.

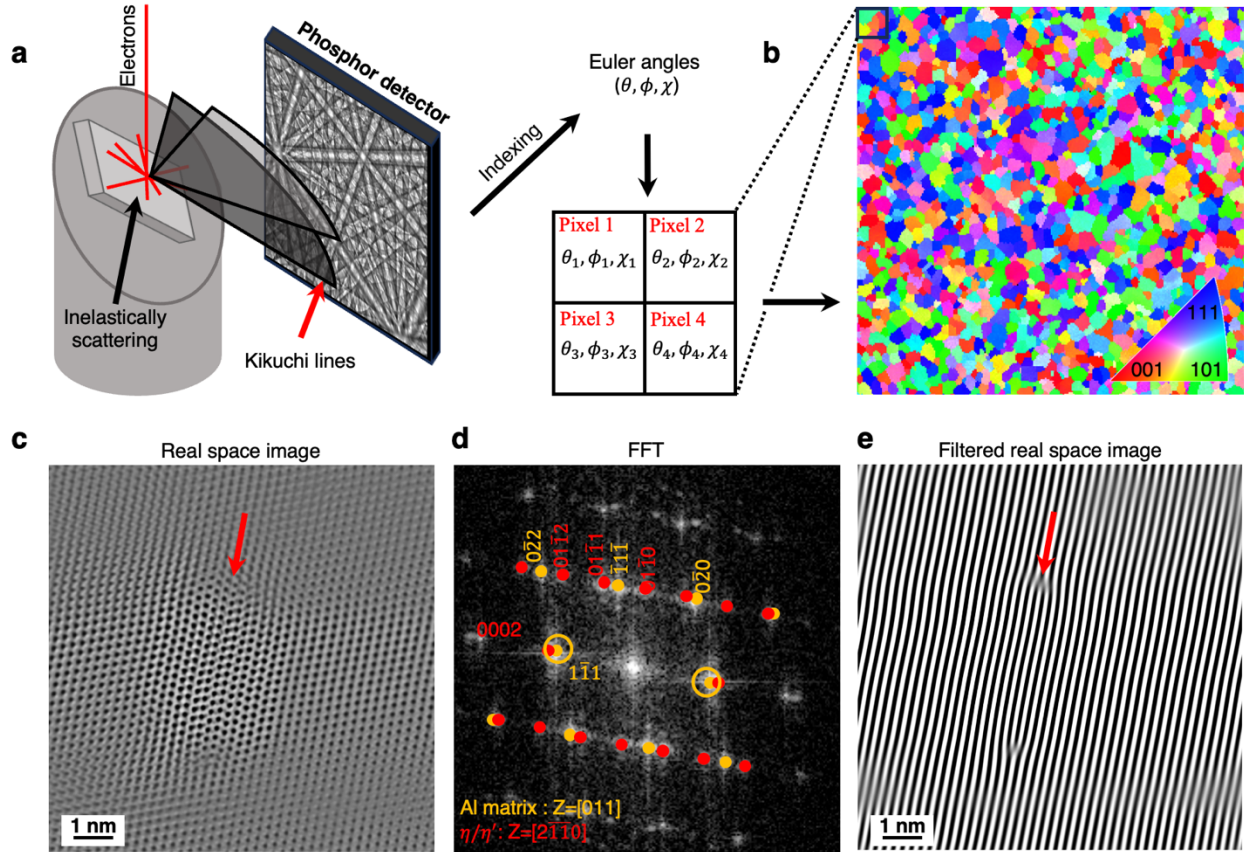


Figure 11 | Schematic of electron backscattered diffraction (EBSD) and TEM FFT filtering.

a Typical geometry of electron backscattered diffraction (EBSD) samples, inclined at 70° from the XY plane. Inelastic scattering is shown to produce multiple diffraction cones that intersect a phosphorus detector and generate Kikuchi bands. **b** Signal is collected step by step on the sample, indexing Euler angles, and slowly creating an orientation map (top right). **c** Dark-field (DF) TEM image showing a semi coherent precipitate. Red arrow points at a dislocation. **d** Fast Fourier Transform (FFT) of **c** highlighting the relative orientation of the two phases. **e** Inverse FFT only with information contained in the orange circles in **d**. The dislocation is easily detected (red arrow).

The indices are then compared to a database containing thousands of phases with specific orientation signatures, enabling unambiguous indexing of Kikuchi bands and precise determination of grain orientation and crystal phase. This process is repeated step by step over the entire area of interest, recording patterns at each point, and constructing maps like Figure 11b, pixel by pixel. In cases where the electron interaction volume exceeds the size of the microstructural features, EBSD becomes resolution limited [134]. In such cases, Transmission Kikuchi Diffraction (TKD) can be employed. TKD uses thin, electron-transparent samples (typically <200 nm thick), and a phosphorus detector placed beneath the sample to collect transmitted electrons scattering signal. Similarly to EBSD, Kikuchi bands are obtained and indexed. Due to the reduced scattering volume, TKD offers significantly higher spatial resolution—on the order of ~2 nm under optimal conditions.

Transmission electron microscopy (TEM) was used to resolve finer-scale microstructural features including dislocation configurations, stacking faults, and nanoscale precipitates. Both bright-field (BF) and dark-field (DF) imaging modes were employed. Bright-field imaging utilizes phase contrast arising from electron interference between the transmitted and diffracted beams, while dark-field imaging collects signal that has been more strongly scattered, enhancing contrast from defects and ordered phases.

High-resolution scanning TEM (HR-STEM) was used to investigate atomic-scale interface structures and assess coherency across precipitate boundaries. Lattice continuity or mismatch was evaluated by observing atomic plane spacing across interfaces, while relative orientation relationships between phases were obtained through Fast-Fourier Transform (FFT) pattern indexing (Figure 12b, middle image). Inverse FFT (iFFT) analysis was applied to filter specific

$\{hkl\}$ reflections and visualize strain fields, dislocation cores, and stacking faults with enhanced clarity. Figure 12b shows the filtering process used to isolate a dislocation inside a precipitate by iFFT of the circled diffraction spots (orange circles). The lines on the last image represent the respective atomic planes, highlighting deviations from perfect periodicity.

High-angle annular dark-field STEM (HAADF-STEM) imaging was also employed, particularly for Z-contrast compositional mapping. Because HAADF intensity scales approximately with the square of the atomic number (Z), this technique proved useful for visualizing compositional boundaries in multiphase materials—for instance, distinguishing tungsten from its borides, or aluminum matrix from its Mg-, Zn-, and Cu-rich precipitates.

Across all alloy and metal systems studied, the insights gained from electron microscopy were central to understanding the microstructural consequences of rapid solidification, the mechanisms of phase transformation and decomposition, and the evolution of dislocation structures during deformation. By coupling microstructural observation with averaged, diffraction-based structure measurements, electron microscopy provided the spatial and analytical resolution necessary to link local structure to global performance.

Chapter 3. Printability and mechanical properties of L-PBF tungsten

3.1 Introduction

Tungsten has historically proven challenging to print by laser powder-bed-fusion (L-PBF), with no documented crack-free, dense samples in the literature thus far [17,135]. In this chapter, we report a fully dense (>99%), crack free, doped tungsten sample, and discuss the cracking mitigation strategies employed—namely a small amount of doping with boron, and stage heating. The preferential segregation of boron to grain boundaries is shown to increase grain boundary (GB) cohesion and displace oxygen, which is known to form embrittling GB oxides [54,61,63,70]. It is also found that alloying drastically impacts the microstructure, refining the grain structure and promoting the formation of low-angle grain boundaries (LAGBs) and cellular solidification. The reduction of high-angle grain boundary (HAGB) density is shown to be partly responsible for crack mitigation, thus improving tensile properties [19,61–65,70,71]. These findings pave the road for fast, reliable production of components needed in extreme environment applications such as plasma-facing components in fusion reactors.

Tungsten is a refractory metal with a body-centered cubic (BCC) structure that exhibits exceptional properties such as a high melting point (3422°C), high density (19.27g/cm³), and excellent thermal conductivity (175 W m⁻¹ s⁻¹). However, the system is very brittle and has a high ductile-to-brittle transition temperature (DBTT: ~200-400°C, depending on impurity levels), which poses significant challenges for manufacturing via L-PBF. The high cooling rates and thermal gradients (up to 10⁷K/s and 10⁷K/m, respectively) inherent to L-PBF lead to high residual stresses and cracking, the latter being exacerbated by tungsten's susceptibility to embrittling oxides.

The demand for printed tungsten systems come from areas that push the boundaries of materials research. The most notable applications, which leverage the material's ability to work in extreme conditions, span from plasma facing components for fusion applications, to space nuclear propulsion, and defense devices such as armor penetrators [136–140]. The freedom of design inherent to L-PBF has the potential to revolutionize these fields, once the system's properties are fully understood.

L-PBF of tungsten is challenging compared to other 3D printing techniques such as electron beam melting (EBM), mainly due to its much higher temperature gradients and cooling rates. EBM also has the advantage of operating in a vacuum environment, greatly reducing the effects of contaminants such as oxides, which are especially detrimental in pure tungsten. Several strategies have been employed to mitigate cracking. Adjusting the scan strategy, such as rotating the scan vector between layers by 67° , has been shown to reduce the formation of ladder-shaped grains, which act as crack initiation sites [60,61,67,141,142]. This technique helps randomize grain orientation and shape, reducing residual stresses and crack formation. Another approach involves remelting, where each layer is scanned multiple times before recoating with fresh powder. This method can help eliminate columnar grains and suppress longitudinal cracks. However, while the strategy reduces surface roughness and grain size, it does not eliminate cracking.

Preheating the substrate to temperatures up to 1000°C has been shown to reduce the temperature gradient and residual stresses, while also aiming to keep the working temperature above the DBTT of the metal [141]. This approach allows screw dislocations to thermally activate and accommodate plastic deformation during cooling and thermal cycling. Despite these efforts, preheating alone has not been fully effective in preventing cracking.

Alloying tungsten with elements like tantalum, niobium, and rhenium can help reduce cracking by altering its microstructure and mechanical properties. For instance, the addition of Ta has been shown to reduce crack density by modifying grain boundary characteristics and enhancing ductility, though this is often only applicable up to specific concentrations, and is not sufficient to mitigate the printing challenges fully [57,67–70,143].

Microstructure control techniques such as grain shape manipulation and inoculation with nanoparticles have been explored to reduce residual stresses and improve mechanical properties. For instance, a comparison between micro and nano-sized yttrium oxides has been reported. Interestingly, while the micro particles slightly alleviated cracking, the nano particles were much more efficient in doing so; this effect was attributed to the formation of a large percentage of LAGBs in the tungsten matrix (Figure 3 a-c.) [70]. The processing conditions in L-PBF significantly impact the quality of the printed parts; critical parameters include laser power, scan speed, layer thickness, and hatch spacing, which collectively impact the volumetric energy density and subsequently the microstructure and mechanical properties of the material. Achieving full densification without flaws like pores or cracks requires precise control of these parameters, and the identification of a reproducible printability window.

Recent studies have highlighted the importance of maintaining an impurity-free environment during printing, as impurities can significantly raise the DBTT and exacerbate cracking [19,59,60,141]. The presence of oxygen, even in small amounts, can have a detrimental effect on the mechanical properties of tungsten.

While L-PBF offers significant advantages for manufacturing complex tungsten components, it also presents substantial challenges, particularly related to cracking and residual

stresses. The ongoing development in L-PBF techniques and processing conditions holds the potential to unlock new applications for tungsten and its alloys in demanding, and harsh plasma environments.

In this work we aim to address the printability challenges of L-PBF tungsten by employing a combination of electron microscopy (S/TEM, SEM, EBSD), x-ray diffraction (XRD), and high-temperature tensile testing. These techniques will help us understand the microstructural mechanisms responsible for the deformation behavior and failure.

3.2 Experimental details

3.2.1 Powder preparation

The tungsten powder (>99.9%, O=250 ppm) used in this work was purchased from Tekna and has a size distribution of $D_{10}=15\text{ }\mu\text{m}$, $D_{50}=34\text{ }\mu\text{m}$, and $D_{90}=45\text{ }\mu\text{m}$. Boron powder from US research Nanomaterials, Inc with a size of 1-2 μm was also used to dope some of the samples. Two wt.% contents were used, 0.1wt%B and 0.3wt%B. The W-B powders were ball milled mechanically in a hardened steel container at 500rpm for 2 hours. The powders were then annealed to improve flowability.

3.2.2 Processing/printing

The samples were printed using Lawrence Livermore National Laboratory's FLAME system. The printing parameters used are summarized in Table 2. The build chamber was operated in an inert argon environment, with a heating stage capability of 1000°C. Temperatures up to 600°C were used in this study. All samples were printed on pure W substrates.

Table 2 | Tungsten and tungsten-boron printing parameters

	Power (W)	Scan speed (mm/s)	Hatch (μm)	Stage heating (°C)	Boron content (wt.%)	Beam size (μm)
RT W	300, 400, 500	100	100	RT	0	60
Heated W	300, 400, 500	100	100	500	0	60
W01B	200:50:450 [†]	100	100	RT, 500	0,0.1,0.3	60
Tracks	400:50:800	100	N/A	RT,400, 500,600	0.3	70
W03B	500, 600	100	100, 150	600	0.3	70
Tensile dogbone	600	100	150	60	0.3	70

[†]The middle number represents the incremental steps between the bounding numbers (e.g. 10:10:40 → 10,20,30,40).

3.2.3 Microstructure characterization

Post-printing, all samples were removed from the substrate by electric discharge machining (EDM). Metallographic specimens were polished with progressively finer SiC papers (600-1200grit) and then diamond colloidal spray (3, 1, 0.3, and 0.05 μm).

A FEI NOVA nanoSEM 230 was chosen for microstructure characterization. Accelerating voltages ranging between 10-20keV were used, with working distances between 4-10mm. EBSD characterization was carried out using a Bruker eFlash detector, a voltage of 20keV, current of 1.5-12nA, WD of ~18-20mm, and step sizes ranging from 16nm to 5μm, depending on magnification. Dwell times between 5-20ms were used.

Transmission Kikuchi diffraction specimens were prepared by FIB-lift out. Imaging was carried out with the same SEM described above, with an accelerating voltage of 20keV, current of 3nA, WD of ~5mm, step size of 40nm, and dwell times between 5-20ms. All EBSD and TKD data was processed using Bruker's Esprit 2.5 software and the open-source software ATEX.

Bright- and dark-field transmission electron microscopy (TEM) images were acquired at the Molecular Foundry (LBNL) using an FEI Tecnai F20 operated at 200 kV. Electron energy loss spectroscopy (EELS) data were collected at the Molecular Foundry on the TEAM I instrument, a double-aberration-corrected transmission electron microscope equipped with a Gatan Continuum GIF. Spectra were recorded on a post-GIF K3 detector with a dispersion of 1.5 eV per pixel. Spectrum images were acquired using a 50ms dwell time. The spectrometer was operated in dual-EELS mode to simultaneously record both the zero-loss and core-loss regions of the spectrum. Elemental mapping is achieved using the Gatan DigitalMicrograph software.

High-temperature testing was carried out in a custom designed apparatus at Oakridge National Laboratory. Ceramic grips were used to fix the sample in place. The heating chamber was brought to 600°C in an inert environment and allowed to reach equilibrium. Tensile testing was then performed at a strain rate of 5×10^{-5} .

3.3 Results

3.3.1 Printing strategies and microstructures

3.3.1.1 Pure tungsten

A preliminary printability window with the respective relative densities measured is shown in Figure 12a; printing parameters were chosen according to the available literature [19,60,144,145] and optimized for the custom set-up used in this study (see Table 2 for specific parameters). Densification above 98% percent was achieved at room temperature (RT); however, cracks and some left-over large porosities were still present (especially along the build direction, BD). Parameter optimization must consider several aspects to ensure successful printing, including

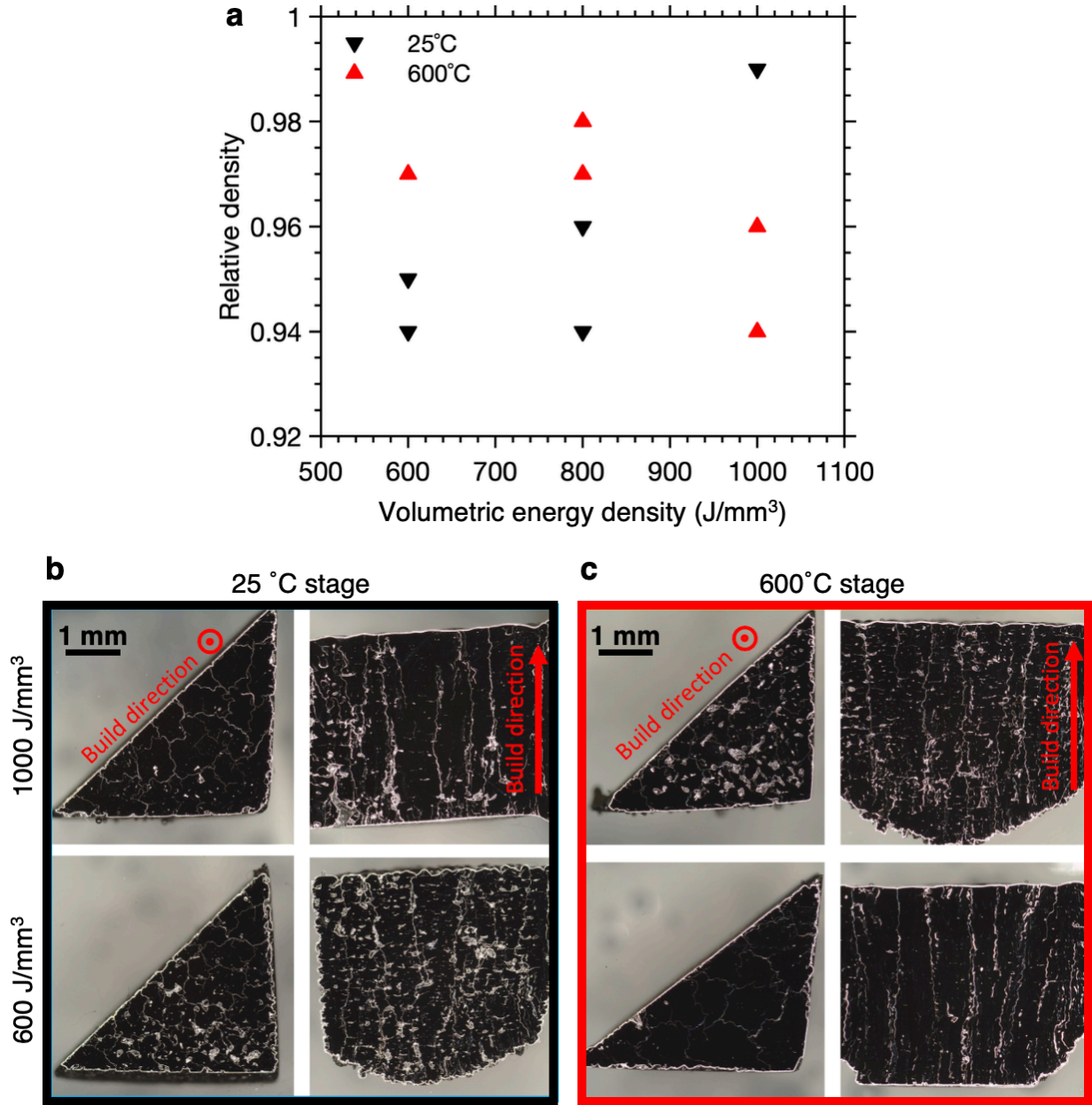


Figure 12 | Density and defects of pure laser powder-bed-fusion (L-PBF) tungsten. **a** Relative density map of pure W samples printed by L-PBF for three energy densities and two stage heating temperatures. **b-c** Optical images of two printed samples showing cracks and porosities along and perpendicular to the build direction (BD).

indirect effects such as powder denudation and spattering. These factors can complicate the melting process by generating defects that affect adjacent laser passes and subsequent powder layers [146,147]. Figure 12b shows two pure W samples printed at room temperature. The effect of volumetric energy density is shown to affect both the cracking behavior and the density, with a porosity difference of about 5%, and more significant cracking present in the lower energy sample.

Aside from parameter optimization, major failure often ensues due to the inability to reliably control oxygen content on the level of parts per million (ppm)-- a common issue with L-PBF technology, where the environment is inert (Argon, N, He, etc.) but not completely devoid of impurities. Additionally, the powders used in this study were not free of oxygen in the as-received state, further complicating oxidation control.

3.3.1.2 Stage heating

To mitigate the cracking phenomenon, stage heating was chosen to minimize stress concentration and cooling rates during solidification, and more importantly, to operate the equipment closer to, and ideally above, the DBTT of tungsten. The exact temperature at which this transition occurs is not agreed upon in the literature, mainly due to the high sensitivity to oxygen impurities of this behavior [19]. Temperatures ranging from RT to 900°C were then tested. Figure 12c showcases an example of how the higher stage heating temperature (and therefore energy) required lower energy densities to achieve dense samples, while simultaneously alleviating the cracking issue. Notice how the 1000J/mm³ sample performs better at RT relative to its 600°C heated counterpart.

Two main factors contribute to printing failures in L-PBF W: the first is strong texture along the build direction (grains growing towards the heat source as more layers are printed on top of

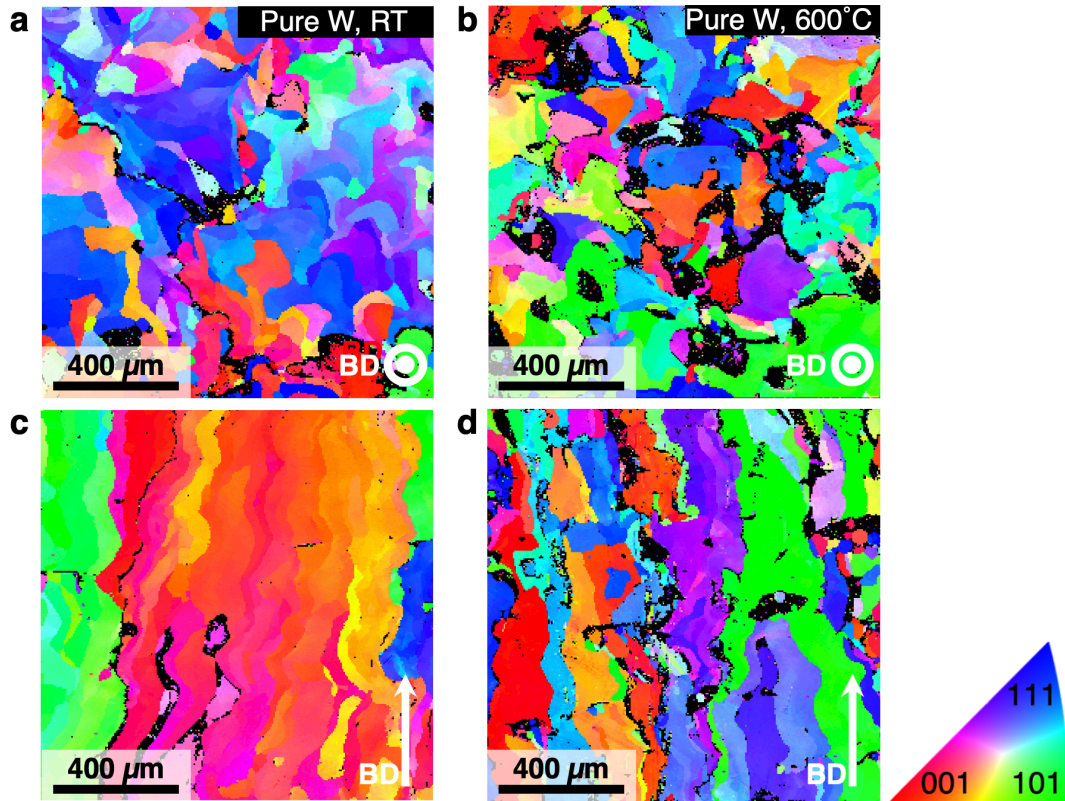


Figure 13 | Electron backscattered diffraction (EBSD) map of printed samples shown in Fig. 12. a, c Texture developed during printing in the room temperature (RT) sample showing strong preferential orientation along the build direction (BD) and perpendicular to it. Cracks along the high angle grain boundaries (HAGBs) are observed. **b, d** Texture mapping of the 600°C sample, showing a slightly more refined microstructure in both directions. Some columnar grains along BD are still present. Cracking is reduced relative to **a**, while some larger porosities are noticeable.

previous ones), as well as oxygen segregation at boundaries, as mentioned above. Electron back-scattered-diffraction (EBSD) was carried out to assess the texture evolution effect in the samples and to verify how microstructural features were affected by stage heating. Figure 13 displays the grain structure of the samples in Figure 12. RT printing resulted in a strong texture, both parallel and perpendicular to the BD. HAGB growing along BD tend to incentivize cracking, as can be seen in both samples, but more noticeably in the RT sample. Stage heating helps to reduce

temperature gradient along BD and thus mitigate the texture. Grains are nonetheless still visibly elongated towards BD; however, smaller, more equiaxed regions are sporadically present as well. HAGBs are often correlated to oxidation-induced cracking, thus, microstructure control is a key step in the elimination of cracks [67,69,143]. As will be discussed in the next session, we also note that the fraction of LAGBs increases slightly due to stage heating, raising from about 58% to 63%. Despite the printing quality improvement, cracking showed to be rather resilient along HAGBs, highlighting the need for a combination of crack suppression techniques.

3.3.2 Effects of boron doping

3.3.2.1 Tungsten + 0.1 wt.% Boron

Many candidates exist in the literature as alloying/doping elements for tungsten, such as niobium, tantalum, and rhenium, amongst many others [67–71,143]. Their microstructural refinement properties are documented for L-PBF W, even though crack suppression was not achieved to date. Our selection process aimed to find an element compatible with irradiation-based applications, such as plasma facing components, while also improving HAGB stability. Boron was found to be the best option, as it is known to improve grain boundary cohesion in W, behaves well when irradiated (at least better compared to low Z elements such as carbon), and has a high affinity

with tungsten, thus potentially suppressing, or reducing, tungsten oxide formation at GBs [148,149].

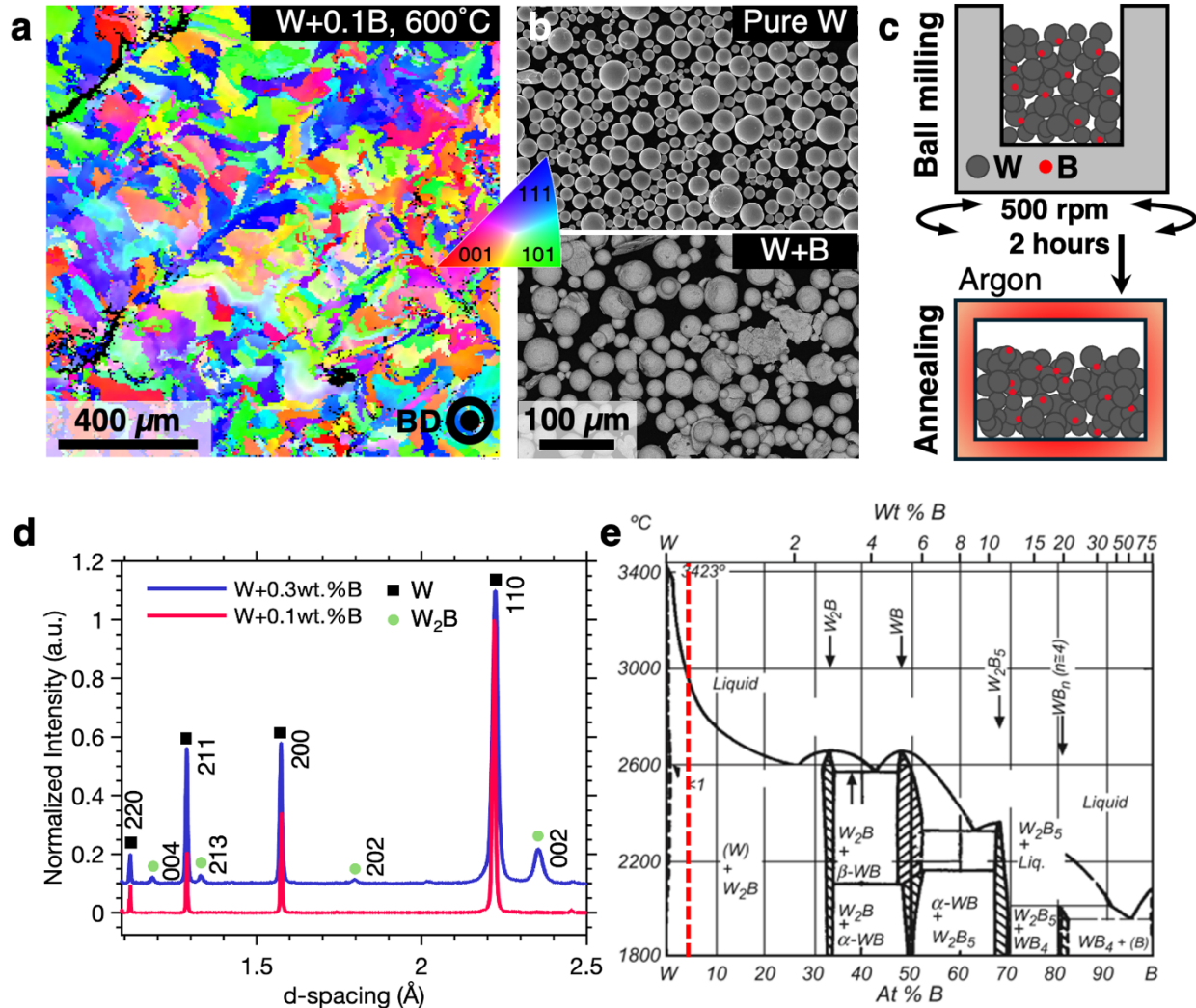


Figure 14 | Effect of boron doping on the microstructure of pure laser powder-bed-fusion (L-PBF) tungsten. a Electron backscattered diffraction (EBSD) map of 0.1 wt.% boron doped sample. **b** Pure W and ball-milled W-B powders. **c** Schematic of ball milling and annealing process used for the powers in **b**. **d** X-ray diffraction spectra comparing boride content as a function of bulk boron composition. W_2B is only detectable in the 0.3 wt.% sample **e** Phase diagram for the W-B system. Red line represents 0.3 wt.% B [150].

A small amount of boron (0.1 wt.%, 1.7 at%) was first chosen to validate the effect of the dopant. This amount was selected to be as close to solid solution as possible, referencing the W-B

phase diagram in Figure 14e [150]; note that the red dashed line marks 0.3 wt.% (~4.5 at. %), which was chosen as the upper bound of B content (discussed in the next section) for this study [150]. The pure tungsten powders were ball-milled in a container with finer B powders (1-2 μm diameter), for 2 hours at 500rpm (Figure 14d). Figure 14 b, c. compares the shape and Z-contrast composition of the pristine powder and its doped equivalent. Spheroidicity was reduced by the milling, although most particles retained their original shaped. This slight morphological change was predicted to affect powder flowability during printing; therefore, an annealing process was adopted after milling to disperse the boron more evenly and improve powder flow [66].

A batch of samples with a variety of printing parameters was printed (see Table 2) and the resulting microstructure is presented in Figure 14a. The microstructure refinement is evident, compared to the pure W samples. No apparent texture was visible in these samples, and their defect concentration (pores, cracks) was almost negligible—a few cracks were still present, however. Boride formation was analyzed via x-ray diffraction (XRD), as seen in Figure 14d (red curve); from the spectrum, no detectable boride peaks were observed, hinting that solid solution was mostly achieved with 0.1wt.%B (within XRD resolution). While it is possible that some borides are present, especially considering that 1.67 at.% B is slightly above the solubility limit displayed in the phase diagram, we note that the high energy laser used for printing likely evaporated boron at a much faster rate than W, thus drastically reducing the B content, and potentially shifting the concentration below the precipitate formation threshold. Scanning electron microscopy (SEM) imaging revealed sporadic segregation of phases—detectable with back-scattered electron (BSE) Z-contrast—mainly along HAGBs.

3.3.2.2 Tungsten + 0.3 wt.% Boron

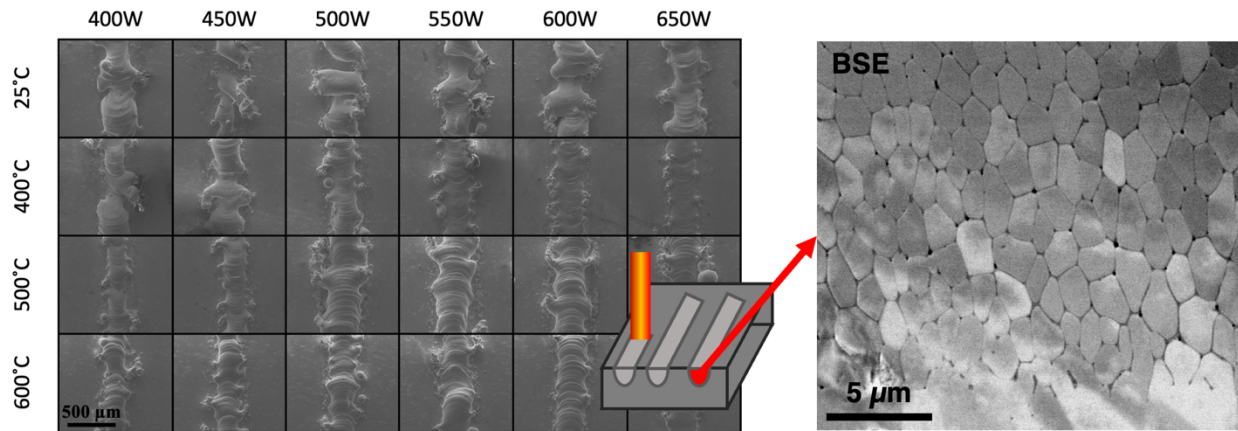


Figure 15 | Single-track parametric study for 0.3wt. %B doping. Top-down view of multiple sets of single tracks printed at different laser powers and stage heating temperatures. Notice that higher temperatures and powers yield smoother tracks without interruptions or balling. The insert shows a cross-sectional backscattered electron (BSE) scanning electron image (SEM) view of one of the tracks (chosen to print bulk samples) showing cellular structure formation in the melt pool, with an average cell size in the range of 1-2 µm.

Despite having initially chosen 0.1wt% B to avoid deteriorating the mechanical properties of the sample via introduction of hard boride particles, the persistent presence (although reduced) of cracks post-printing required a more thorough investigation of the dopant's potential. A concentration of 0.3 wt.% B was then chosen to purposely induce second phase precipitation—ideally reducing oxidation of tungsten in favor of borides. To ensure optimal parameters and to properly monitor the microstructural changes due to the higher B content, a parametric single-track study (Figure 15) was designed. The aim of this step was to select printing conditions that resulted in smooth laser tracks with substantial grain refinement and boride precipitation, while suppressing cracks. Surprisingly, none of the tracks developed cracks. Cross-sections were then analyzed under SEM as shown by the BSE image and the schematic in Figure 15b. The melt pool boundary is visible at the bottom of the image and coincides with the termination of the fine, equiaxed cellular

structure observed throughout. The parameters used to obtain this microstructure were chosen to print bulk samples. Z-contrast is also visible around the cells, showing that lower Z elements (B) are present in the form of precipitates. This was confirmed in the XRD in Figure 14d (blue line), which displays the indexed second phase (W_2B) peaks. We note that Z-contrast alone is not sufficient to identify specific elements, but rather it only carries information regarding relative Z numbers. The darker phases in Figure 15 could thus theoretically be oxides; however, since these phases became prominent only after adding more boron to the system, and given that their manifestation coincides with the appearance of second phase peaks in XRD, we assume that the segregations around the cellular structures are indeed borides. This assumption is verified in the next section via transmission electron microscopy (TEM).

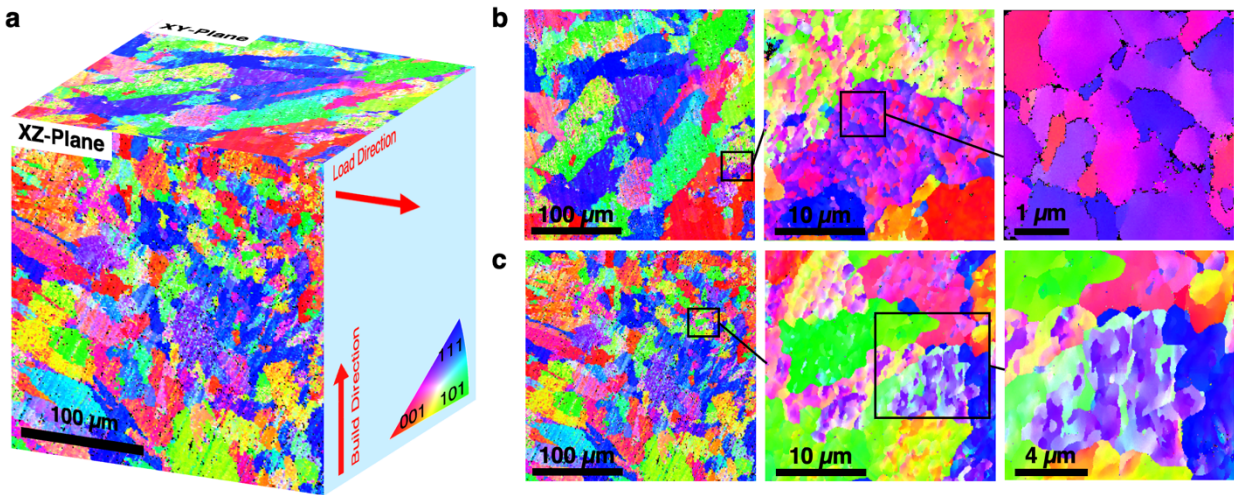


Figure 16 | Electron backscatter diffraction (EBSD) of a fully dense, crack-free bulk sample printed with 0.3 wt.%B. a XY and XZ planes of the bulk sample, oriented relative to build and loading direction **b, c.** Higher magnification of the same maps shown in **a**, highlighting the microstructural refinement effect and the local low angle misorientation associated with cellular structures.

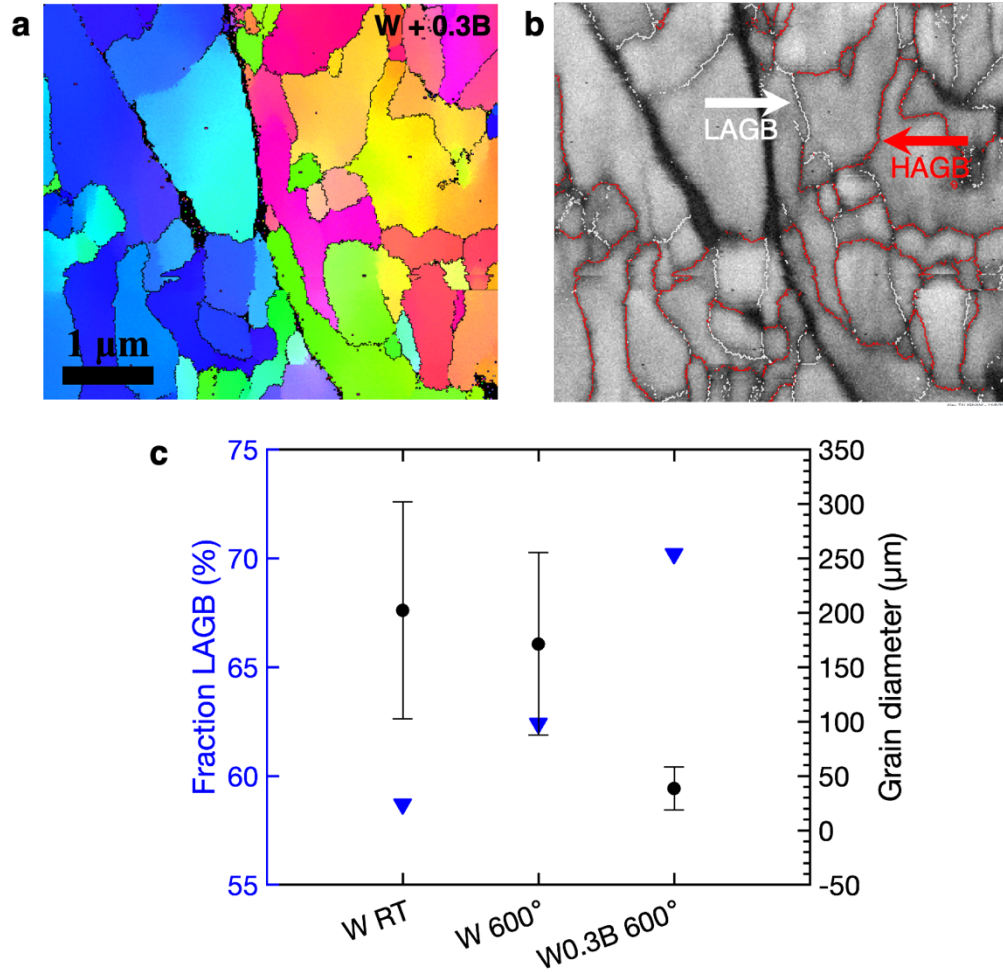


Figure 17 | Grain boundary evolution and grain refinement effect of boron doping and stage heating strategies. **a** High magnification EBSD map of W0.3B bulk sample showing small areas of misalignment that coincided with cellular structure. Submicron features are present as well. **b** Image quality (IQ) map of the same region in **a**, showing LAGB and HAGBs in white and red, respectively. **c** Bulk statistics showing trends for grain boundary refinement and LAGB evolution across the three samples discussed thus far.

Bulk samples were subsequently printed according to the optimized single-track parameters; near fully dense, completely crack-free components were obtained. The sample's microstructure is shown in Figure 16. EBSD was taken both along the BD and perpendicular to it; showing evidence, similarly to W0.1B, that boron refined the microstructure substantially. Additionally, large quantities of LAGBs were formed with the higher B content. Higher

magnification regions reveal a refined microstructure heavily decorated with LAGBs. This detail is in accordance with the results obtained in the single-track studies, where micron sized cells are observed. Quantification of the LAGB formation effect is displayed in Figure 17c. Notice that the LAGB content grows to above 70% in W0.3B, about a 20% increase from the first batch of pure W samples. Significant grain size refinement relative to the pure W samples is also presented. Figure 17a shows a high magnification EBSD map of the bulk sample, showing a large quantity of local misorientation on the order of 1-2 microns. Notice that many submicron features are also present. Figure 17b presents an image quality map of the same region, with overlaid LAGB and HAGBs (white and red arrows respectively).

3.3.3 High temperature tensile properties

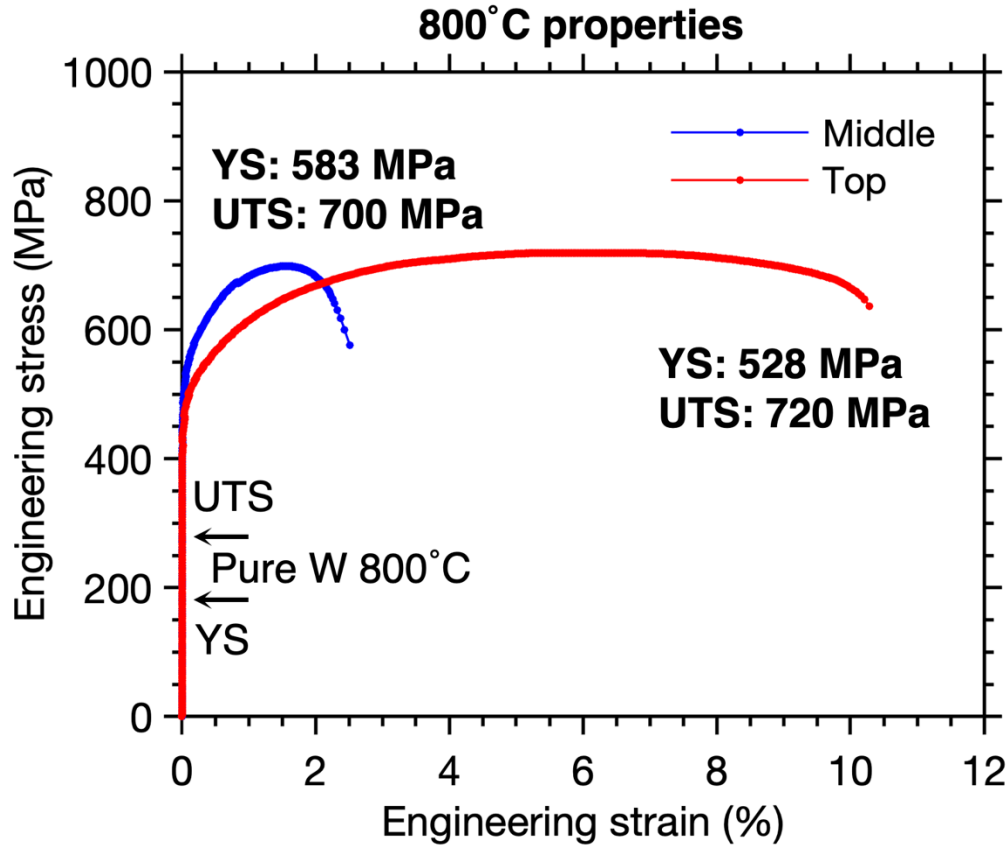


Figure 18 | 800°C tensile properties for two W0.3B samples. The black arrows compare YS and UTS of tensile properties reported for pure W printed via EBM [151].

Following successful printing of W0.3B, two dogbone tensile specimens were prepared for high temperature testing; the mechanical properties at 800°C are shown in Figure 18 [151]. The two samples have yield strengths (YS) of 583 MPa and 528 MPa respectively, with ultimate tensile strengths (UTS) of 700 MPa and 720 MPa. Because only two samples were tested, the variability in elongation at fracture is significant, with the less ductile sample only reaching about 3% elongation at failure, as opposed to ~11% in the second sample (red curve). This difference is likely due to defect-driven failure, introduced either during printing or manufacturing of the tensile test specimens. Alternatively, a location-dependence of the samples might be present and playing a role in the defect density. The terms ‘top’ and ‘bottom’ refer to the regions of the bulk sample

from which tensile dogbones were manufactured—bottom being closer to the substrate. A difference in cooling rates may have introduced more defects closer to the substrate, where cooling tends to be slightly faster due to faster heat dissipation. More samples will need to be prepared in future work to obtain more representative properties. For reference, the only other 3D printed W tensile properties available in the literature (printed via electron beam melting (EBM), rather than L-PBF), are shown by the black arrows in Figure 18 [151]. It is evident that the sample in this work achieved significantly higher strength values, partly owing to the introduction of boron and the resulting second phase formation.

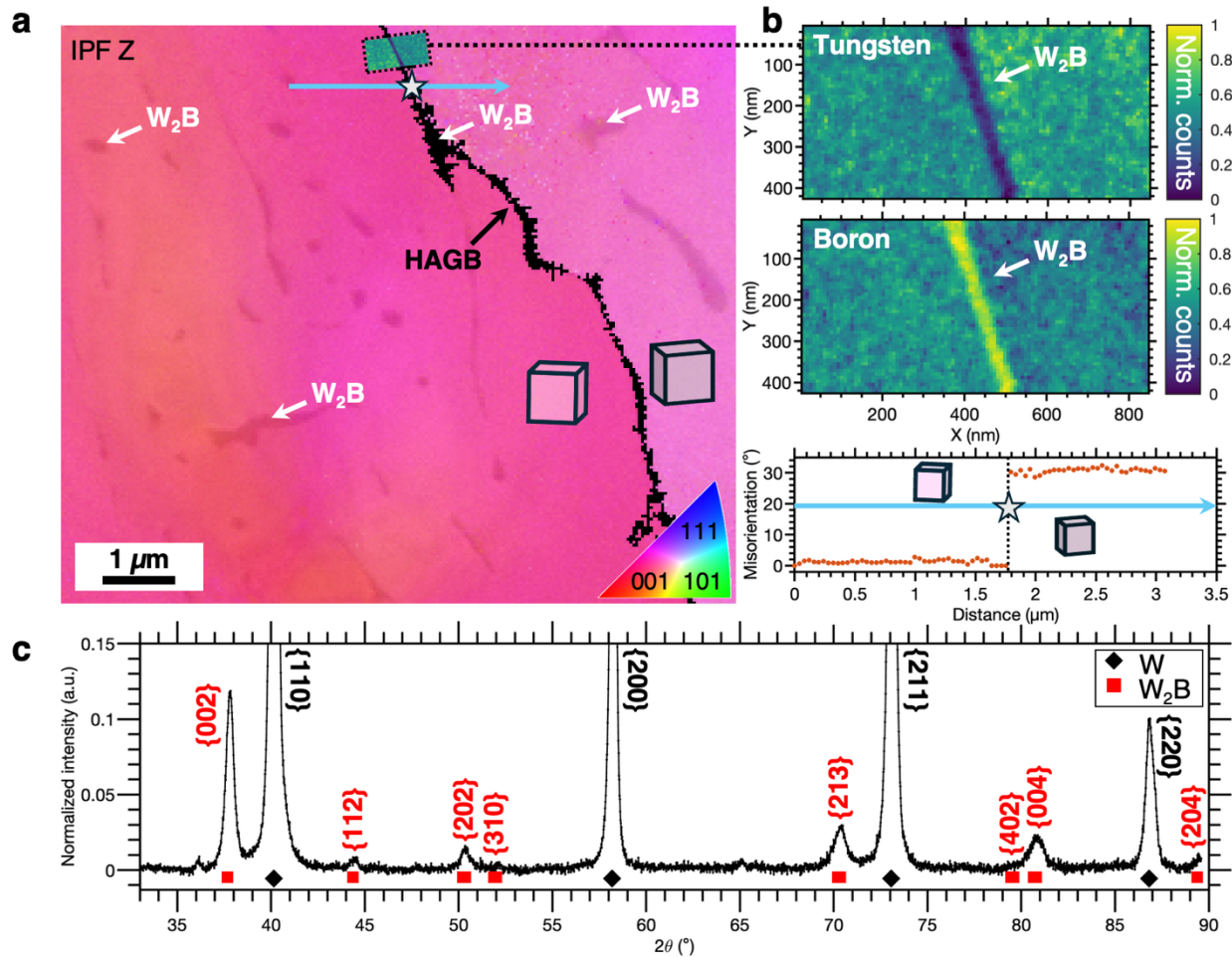


Figure 19 | Phase/chemical analysis of boron precipitates in W0.3B sample. a Transmission Kikuchi Diffraction (TKD) map of W0.3B sample. Precipitates are visible both at high angle grain boundaries (HAGB) and surrounding low angle grain boundaries (LAGBs). **b** Electron energy loss spectroscopy (EELS) of the GB shown in **a** showing boron segregation at boundary. Below it is a misorientation map showing the angle between the two grains in **a**, marked by a star and arrow. **c** XRD spectra with indexed phases (W, W₂B).

Figure 19 leverages Transmission Kikuchi Diffraction (TKD) mapping of the undeformed ‘top’ specimen shown in Figure 18. The sample was lifted using a focused ion beam (FIB) from the dogbone, purposely including a HAGB to verify the composition and locations of precipitates. A misorientation plot shows the nature of the grain boundary marked by the white star—the angle between grains is approximately 35° (Figure 19c).

From electron energy loss spectroscopy (EELS, Figure 19 b) the presence of boron at the boundary is confirmed. This signal was rather weak due to sample thickness under TEM; thus, we refrain from drawing quantitative conclusions from these maps, and instead simply highlight the trends of increasing B content at the boundary. Not displayed in the image, due to weaker signal, is the equivalent oxygen map. We note that oxygen appeared to be present at the boundary, alongside B. Further investigation is needed to properly assess the amount relative to boron and whether there is preferential segregation at HAGB vs LAGB. Sample oxidation due to exposure to air after FIB also complicates proper elemental quantification. A higher resolution XRD spectrum of the sample is lastly shown in Figure 19d. Indexing indicates that the original assumption that the borides are primarily W_2B appears to be accurate, as shown by the respective indexed planes. From Figure 19a it is also apparent that W_2B segregates everywhere in the sample, not just at boundaries, but at grain interiors as well; their even dispersion is believed to contribute significantly to the high YS shown in Figure 18.

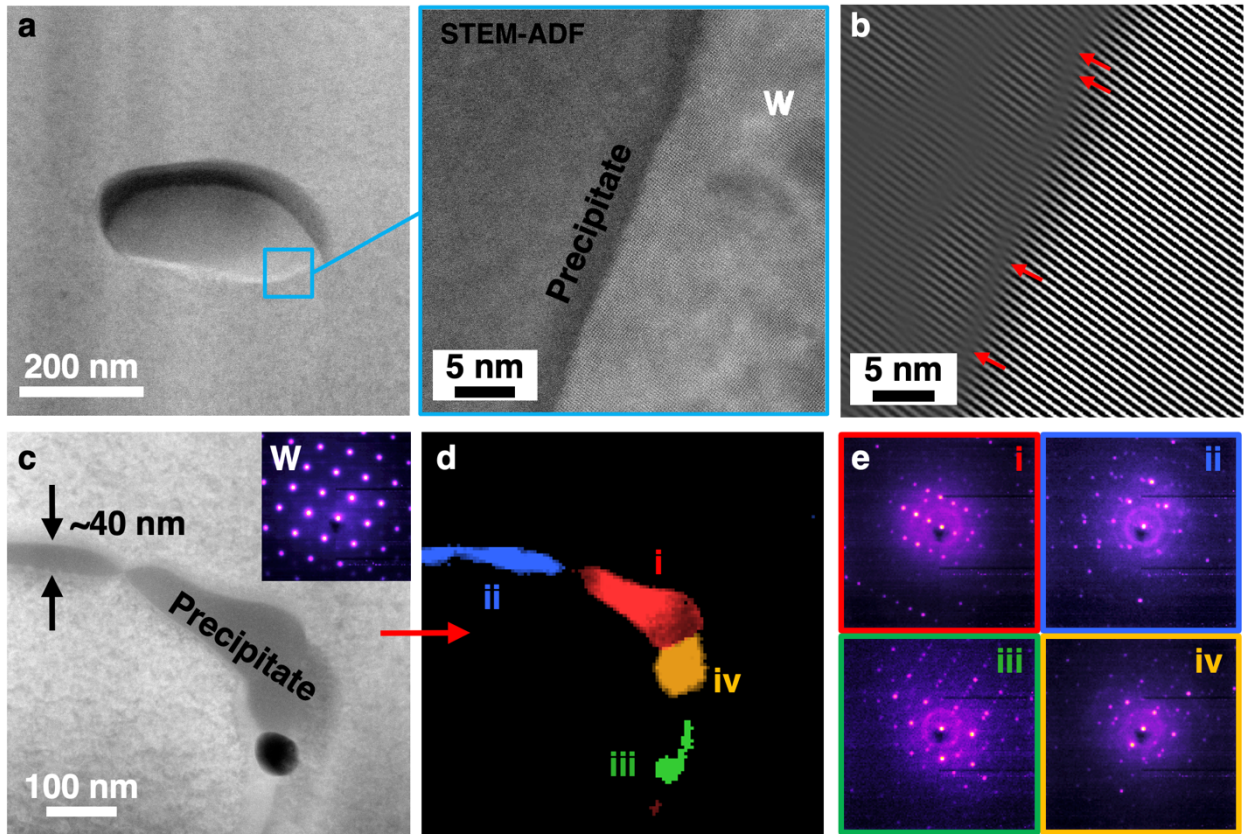


Figure 20 | Transmission electron microscopy analysis of undeformed and deformed high ductility sample. **a** Precipitate in the undeformed sample. The insert shows a STEM HAADF higher magnification image of the precipitate/matrix interface **b** Filtered FFT of **a** dislocations are highlighted by red arrows. **c** LAGB precipitate in the post-mortem sample, insert is a diffraction pattern collected from the surrounding W matrix. **d** Color-coded map of **c**, each color represents a different crystallographic orientation. **e** Diffraction patterns collected for each region in **d**.

High resolution TEM was used to further investigate the nature of the precipitates and their role in deformation. Figure 20 analyses finer microstructural details of the higher ductility sample in both the undeformed and post-mortem state. Figure 20a-b shows TEM of a precipitate in the undeformed state, with a higher magnification image of the boundary between W and the particle. By filtering the image's Fast Fourier Transform (FFT), interface dislocations were revealed (red arrows), suggesting that precipitates are not fully coherent with the matrix, thus likely resisting plastic deformation by dislocation accumulation at the interface. Figure 20c shows another LAGB

precipitate, in the same sample, post tensile deformation. The insert diffraction pattern is collected from the surrounding matrix and is indexed to match $Z = [110]$ for BCC. Figure 20d-e displays a map of the same precipitate color-coded with respect to its crystallographic orientation. Surprisingly, the precipitate appears to be subdivided into differently orientated regions; diffraction patterns collected via 4D STEM are shown in e. Further investigation is needed to assess whether the segmented nature of the precipitate is a result of printing or deformation. In either scenario, the borides' ability to accommodate deformation without cracking may partially explain the excellent tensile properties in Figure 18.

3.4 Discussion

3.4.1 Crack mitigation

This chapter investigates the mechanisms responsible for the well-documented difficulty in printing L-PBF W [17]. Two key factors that dominate the cracking phenomena are presented, namely oxidation prevention and texture randomization/refinement. This strategy is achieved via a combination of stage heating and doping; as a result, printing becomes feasible even when strict control of oxygen impurities is not available. Through optimization of bulk printing parameters and parametric single-track studies, we identified printability ranges that can withstand printing as well as subsequent tensile testing. The latter aspect is crucial in the refractory L-PBF field, since obtaining tensile data implies a lack of micro and macro cracks/defects in the bulk samples. To date, no literature has reported bulk tensile properties for tungsten-based L-PBF systems [17].

Figure 21 offers a schematic view of the four steps presented in this work. From left to right, pure W printed without any stage heating results in large, columnar grains with strong texture. Embrittling oxides form at HAGBs and cause them to crack during printing [60,152]. By heating

the build stage, some texture randomization is achieved and some cracks are suppressed, this effect is in part due to a reduction in the thermal gradients generated, which are diminished by about 600°C. Additionally, the higher stage temperature is closer, if not higher, to the DBTT of the system, allowing for more plastic deformation during printing without catastrophic failure. In an oxygen free sample, 600°C heating would likely be enough to confidently exceed the DBTT of W, potentially preventing cracks from forming even without the addition of doping elements. Because oxygen control tends to be worse in L-PBF, compared to techniques that require vacuumed build chambers (e.g. EBM), additional steps had to be taken to prevent oxidation [151]. The third schematic highlights two key points: boron doping refines grain size significantly, and few borides are formed in the process. Oxidation is likely dramatically suppressed, as some of the boron segregates to the boundaries, improving their cohesion, and displacing oxygen [148,149]. These benefits, coupled with stage heating, eliminate most of the cracks, but do not completely suppress them. Lastly, by introducing 0.3wt.% B and keeping stage heating constant, large amounts of borides form throughout the microstructure, both at LAGB, HAGBs, and grain interiors. Many borides are found surrounding BCC-W cellular structures, creating a network of fine cells on the order of 1.7 μm . Oxidation is suppressed further, or more strongly counteracted by the large presence of B and its borides. The microstructure is refined further, with LAGB fraction increasing past 70%.

3.4.2 Precipitation behavior

In most systems that rely on ceramic particles (oxide, boride, carbides) to refine microstructural features, the particles act as nucleation sites during solidification. This is effective in part due to the ceramics having much higher melting points than the surrounding metal matrix;

consequently, the particles solidify first, followed by the surrounding matrix, which turns to a solid phase around them. In the W-B system, the process does not unfold in the same way.

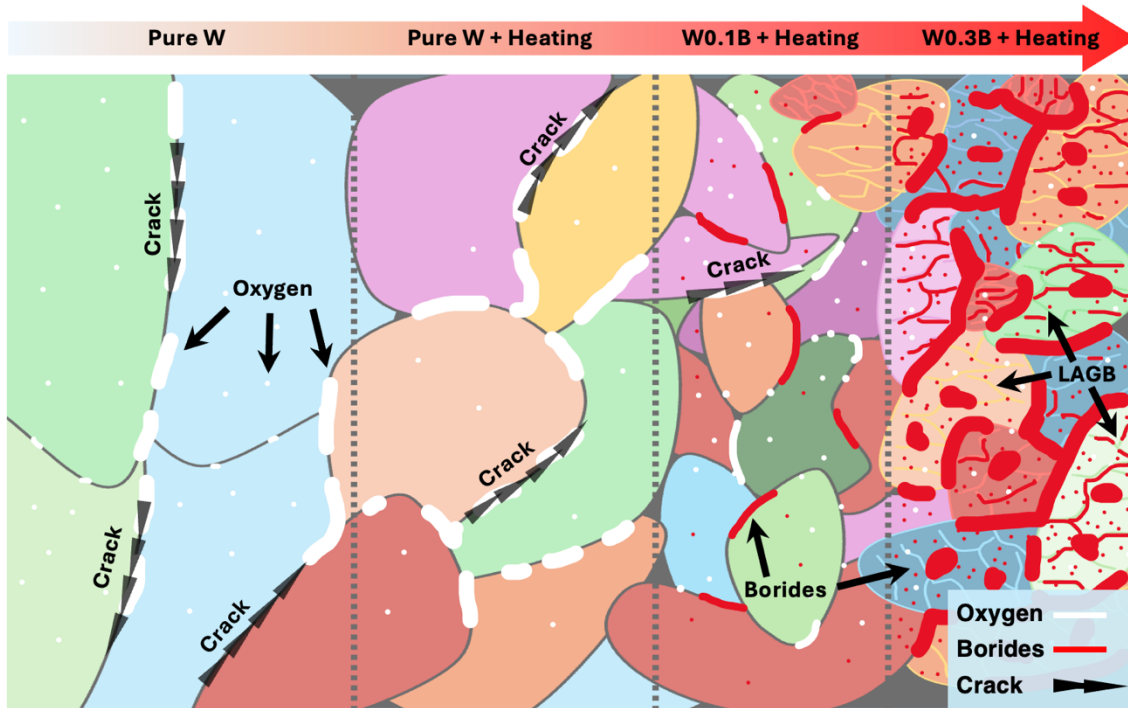


Figure 21 | Schematic of microstructure evolution across four conditions used in this work to print laser powder-bed-fusion (L-PBF) tungsten. Cracking is reduced and eventually suppressed with a combination of boron inoculation and stage heating. Notice how borides only form significantly after 0.3 wt.% B is introduced, effectively displacing oxygen and improving grain boundary cohesion.

The W-B phase diagram displayed in Figure 14 shows that the melting temperature of W_2B is roughly $700^\circ C$ lower than pure W. As a result, even if W_2B is present in the powder before printing (ball milling could induce the second phase formation), it will likely melt much more readily than the W matrix when exposed to the laser.

During cooling, W solidifies first, given its higher melting temperature [148,150,153]. Because boron has low solubility in W, it is rejected into the liquid during solidification, rapidly

raising local B concentration at the solid-liquid interface. This favors the formation of BCC-W cellular structures surrounded by W₂B nano-layers (Figure 15b). Rapid solidification induced by L-PBF tends to create large internal stresses that are partly accommodated by misaligning the cells relative to one another. The effect is seen in under EBSD as small local crystallographic misorientations between neighboring cells. Overlapping laser scans and repeated melting of subsequent layers amplifies the effect, as the metal contracts and expands cyclically and thus deforms plastically. Cracking may then be further suppressed by this process, as the matrix has an alternative venue for plastic deformation before fracture ensues.

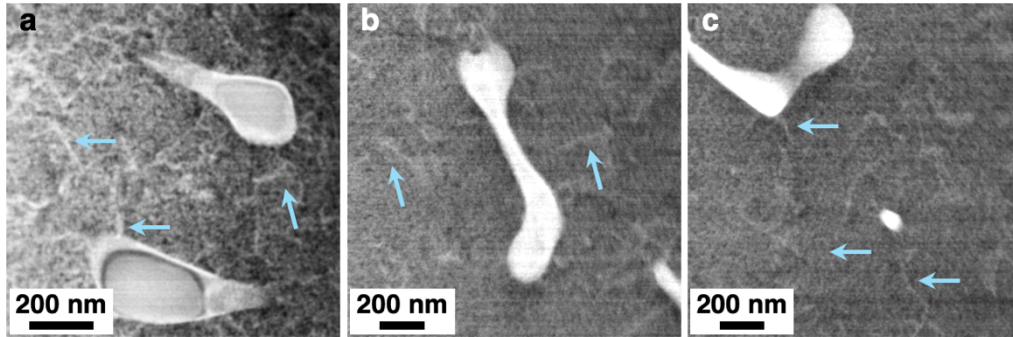
3.4.3 Deformation mechanisms

The mechanical properties in Figure 18 are promising for extreme environment applications. Two contributions are briefly discussed relative to the literature: dislocation strengthening and boundary strengthening.

Dislocations mainly arise from the printing process; considering L-PBF's high cooling rates and cyclical thermal history, the dislocation density is expected to be significantly higher than an equivalent manufactured via EBM. SXR D will be used to quantify exact values in future work. Second, as discussed earlier, the introduction of boron results in more than a two-fold increase in YS of the metal. Analysis of the microstructure shows that cells form homogeneously throughout

the sample, with a rough cell size of $1.7\ \mu\text{m}$ in diameter. Even though borides appear to

Deformed TEM



Fracture surface SEM

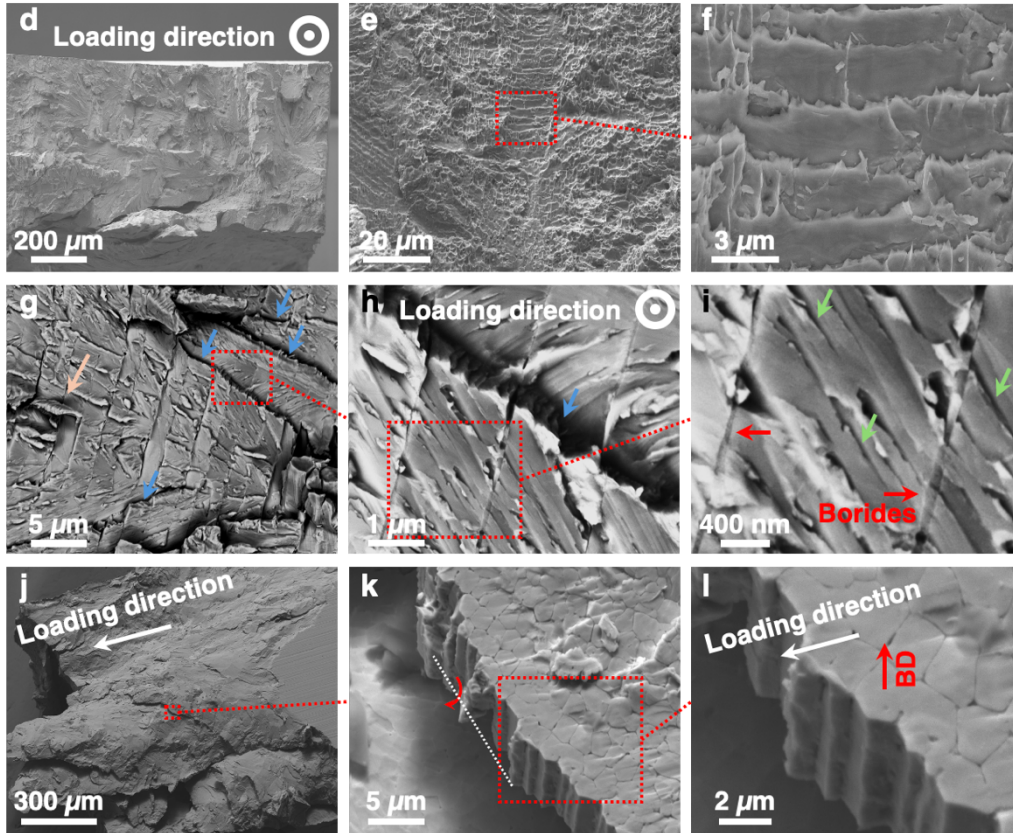


Figure 22 | Fracture surface and deformed microstructure. a-c Transmission electron microscope (TEM) images showing dislocation interaction (light blue arrows) and borides. d-f Head on view of tensile specimen fracture surface revealing features that suggest ductility, some dimpling is visible. g-i Cell walls surrounded by borides are visible, shearing within cell interiors appears to form at 45 degrees relative to the cell long axis. Minimal deformation is seen at the boride boundaries. j-l Tilted fracture surface revealing the cells' preference to delaminate at the boundaries, rather than fracturing or breaking.

form at HAGBs as well as LAGBs, the smaller scale dominates the grain boundary effect. Little data is available regarding the GB strengthening effect at elevated temperature—we therefore refrain from quantitatively assessing the strengthening contribution of the mechanism, but point out that relative to pure W EBM, the introduction of boron appears to increase strength by a few hundred MPa, the effect is attributed to the cellular structure surrounded by borides.

Despite the high yield strength, elongation at fracture surpassed 10% in W0.3B. The literature for pure W shows elongations exceeding 30%, although at the cost of much lower YS, as dictated by the well-known stress-strain tradeoff [151]. Figure 22 presents microstructural features of the post-mortem W0.3B sample. The top row shows the presence of dislocations interacting with the precipitates (light blue arrows), highlighting the effects of strain hardening as the material is loaded in tension. Precipitates do not appear to shear visibly, suggesting that the treatment of cell walls as grain boundaries is valid.

SEM images showing the fracture surface of the high ductility sample offer some insight into the mechanics of deformation: the system shows signs of both ductile and brittle fracture, depending on the location. Figure 22 d-f show dimpling, which is prevalently found on the surfaces with normal parallel to the loading direction—their presence suggests high local plasticity. G-i are taken from a region that appears more brittle. We note however that the surface is not as flat as typically found in brittle metals/ceramics, but rather it shows step-like features (dark blue arrows) that correspond to sheets of cellular structures breaking apart. In the magnified images, large

plastic deformation is found between cellular structures (green arrows), and each cell is bounded by boride precipitates (red arrows). The salmon-colored arrow highlights one of the steps, showing signs of delamination and bending away from the plane.

Figure 22 j-l shows another example of cell delamination. The solidification direction of the cell is visible, with the longer axis of the cylindrical structure parallel to the build direction. The cells favor separation along the boride boundaries, rather than fracturing internally. Borides seem to withstand the stress state and keep their wall shape. However, the cell interior shows massive plastic activity, with shear bands visible at 45 degrees to the long axis of the cell. This behavior implies that cells do in fact deform internally and dislocations are forced to pile up at the boride interface. At the same time, EBSD revealed that slight misalignments between neighboring cells exist throughout the matrix, implying their motion is limited, but not absent. During loading the cells accommodate more plastic deformation by taking advantage of this process, thus improving ductility while the cell interiors keep deforming and contributing to work hardening.

3.5 Summary and future work

In this work we used a combination of stage heating, which reduces residual stress and thermal gradients, in combination with a B-doping strategy, to enable L-PBF of bulk, dense, and crack-free tungsten. The mechanical properties at 800°C were found to exceed the strength of similar (pure) systems, while retaining over 10% elongation to failure. The microstructural refinement of boron was shown on multiple length scales; dense cellular structures surrounded by tungsten borides formed throughout the sample, strengthening the metal by a Hall-Petch -like mechanism at the cell level. TEM and EBSD revealed the cellular structures' ability to locally misorient to accommodate plastic deformation during printing and tensile loading. Evidence of

cell interior shearing was found on the fracture surface of the tested samples, suggesting that boride cell walls act as strong barriers. While the walls retain their shape overall, TEM shows that their orientation can vary locally, creating nano-sized regions with different crystallographic orientation. The coexistence of these mechanisms is found to partly explain the high strength and ductility of the material.

Boron is assumed to replace oxygen along HAGBs, which otherwise tends to form embrittling oxides that are prone to cracking. Further investigation into the thermodynamics and kinetics of this process is planned for future work: first principles calculations are needed to confirm boron's affinity to oxygen relative to tungsten's. Higher resolution TEM is also planned to reveal the exact nature of the dislocation interactions with cell walls, confirming pileups at boundaries and the resulting deformation, or lack thereof, of the boride walls. Lastly, SXR is planned to get higher resolution, statistical data regarding dislocation densities and exact boride fraction.

Chapter 4. Mechanical properties and deformation mechanisms of L-PBF Al-Mg-Zn-Cu alloys

4.1 Introduction

4.1.1 Overview and objective

Additive manufacturing (AM) has gained momentum in aerospace and automotive sectors for its ability to produce net-shape components with mechanical properties that often exceed those of conventionally manufactured alloys. Laser powder-bed-fusion (L-PBF), a leading AM technique, leverages high cooling rates to generate fine, hierarchical microstructures. However, the 7xxx-series aluminum alloys have long been considered ‘unprintable’ due to hot tear cracking.

Recent work has overcome this limitation and enabled crack-free processing by modifying solidification pathways. TiC nanoparticles can act as heterogeneous nucleation sites [20,41,45–47], suppress columnar/dendritic growth, and promote an ultrafine, equiaxed grain structure while simultaneously pinning grain boundaries during subsequent thermal exposure. However, the mechanisms by which TiC-modified solidification and post-processing translate into mechanical properties are still not well understood.

In this chapter, we investigate a TiC-inoculated L-PBF Al-Mg-Zn-Cu alloy processed in three states: as-printed (AP), hot-isostatically pressed (HIP), and HIP + T6 aged (H6). We show that TiC-assisted solidification, followed by HIP and peak aging, produces a TiC-stabilized fine grain structure surrounded by a grain-boundary η “cage” and a dense intragranular network of η' precipitates and solute-rich clusters. The resulting H6 condition exhibits, to our knowledge, the highest specific ultimate tensile strength (SUTS) reported for any AM 7xxx-series alloy, while

simultaneously achieving high ductility (~7.5%). Its SUTS surpasses that of conventionally manufactured Ti-6Al-4V, a benchmark lightweight structural alloy.

Here, we combine in-situ synchrotron X-ray diffraction (SXRD) with transmission electron microscopy (TEM) across all three processing states to unravel the relationship between solidification, microstructure, and tensile mechanical response. We show that TiC-induced dendrite suppression and grain-boundary pinning give rise to a grain boundary (GB) ‘cage’ effect, which drastically improves the strength of the alloys. Subsequent HIP treatments can be engineered to refine the cage effect by redistributing GB precipitates, substantially improving work-hardening potential and uniform elongation, while retaining high stress values. We also show that peak age hardening treatments introduce intragranular, nanoscale η' precipitates, which facilitate load redistribution from grain boundaries into the grain interiors. This dual-level strengthening—boundary cage effect, coupled with intragranular nanoscale obstacles—explains the alloy’s simultaneous strength and ductility, thus reframing nanoparticle inoculation as a route for both printability and microstructure-property optimization in AM high-strength aluminum alloys.

4.1.2 Background

High strength aluminum alloys (7xxx, 6xxx, or 2xxx series) are essential in light-weight structural applications in the automotive and aerospace industries [18,23,29,47,154–156]. These alloys (especially 7xxx series) suffer from what is known as ‘hot tear cracking,’ a dynamic process responsible for local chemical heterogeneity that incentivize crack formation and propagation of cracks upon cooling [18,41,42,46]. This phenomenon is amplified in the presence of extreme temperature gradients and cooling rates, typical of laser powder-bed-fusion (L-PBF) processes

[11,14,18,20,24,38,73,97]. The cracking phenomenon stems from the formation of columnar/dendritic structures at the liquid-solid interface of the alloy. Local undercooling forms trapped liquid pockets between dendrites, and subsequent thermal cycling of these regions leads to large, localized stresses that promote cracking.

Recent efforts have mitigated the hot tear cracking issue by introducing nano-sized inoculants into the alloy powders. Nanoparticles hinder the formation of dendritic structures by decreasing the degree of undercooling enough to achieve an equiaxed microstructure, effectively solving the printability challenge [18,20,38,41,46,50,157]. In the present system, TiC nanoparticles play a dual role: during solidification they promote a very fine, equiaxed, nearly random grain structure, and during subsequent heat treatments they pin grain boundaries, suppressing grain growth and stabilizing the fine microstructure. While these effects resolve the printability challenge, the consequences of TiC-modified solidification for strengthening mechanisms in AM Al-Zn-Mg-Cu alloys remain only partially understood.

AM materials often exhibit microstructures and properties that vary drastically from their cast and wrought counterparts. Extreme printing environments often lead to finer microstructures, non-equilibrium signatures such as dislocations, intermediate phases, vacancy clusters and chemical segregation [11,14,18,24,38,43,73,97]. In high-strength 7xxx alloys, multiple strengthening mechanisms can be active simultaneously: grain-boundary strengthening, solid-solution strengthening, dislocation strengthening, classical precipitation strengthening (via η' and η) [12,18,26,29,34,38,55,75,76,82–86,154,155,158,159]. More recently, the concept of cluster strengthening has also emerged as an excellent venue for mechanical property enhancement on the

nanoscale, although highlighting the difficulty in decoupling the individual strengthening effects in complex, multi-phase systems [75,76,85,154,155].

In this work, we use a combination of in-situ SXRD and state-of-the-art high-resolution TEM to unravel the deformation behavior of a TiC-inoculated L-PBF Al-Mg-Zn-Cu alloy. Diffraction peaks from the matrix, Mg- and Zn-rich precipitates, and TiC are tracked respectively during uniaxial tensile loading, revealing how load is partitioned among these phases. In-situ lattice-strain and peak-broadening analyses are used to follow grain-family-specific deformation and dislocation evolution, while complementary TEM and STEM-EDS/FFT analyses characterize the nanoscale precipitate and solute-rich regions before and after deformation. By systematically comparing AP, HIP, and H6 states, we link solidification control, heat treatment, and nanoscale chemical heterogeneity to the observed strength-ductility trade-offs. We show that a TiC-stabilized GB η cage effect provides a common strengthening baseline in HIP and H6, and that the introduction of a dense intragranular η' /cluster network in H6 both increases yield strength and redistributes plasticity into the grain interior, enabling the exceptional specific ultimate strength and ductility reported in this chapter.

4.2 Experimental details

4.2.1 Feedstock material

The feedstock powder used in this work is a 7xxx series aluminum inoculated with TiC nanoparticles (NP), named AA7075 herein, manufactured by Metali LLC (USA). The powder morphology was examined by a scanning electron microscope (SEM, Zeiss Supra 40VP). The powder surface is partially covered by TiC nanoparticles; additionally, we note that due to the manufacturing method of the AA7075 powder [47], the TiC nanoparticles are well dispersed both

on the surface of the particles, as well as in their interior. The as received AA7075 powder has D₁₀, D₅₀, and D₉₀ of 13.8 μm , 39.6 μm , and 56.0 μm , respectively.

The chemical composition of the AA7075 powder was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), as shown in Table 3. For comparison, the composition of a commercial, wrought 7075 (McMaster-Carr) sample was also analyzed. The values in the brackets are the common compositional ranges for aluminum 7075. We note here that the powder contains a significantly elevated amount of Zn and Mg; the excess is designed to help form grain boundary “cage” structure and counteract the loss of material caused by laser-induced evaporation during the L-PBF process. Lastly, since carbon could not be isolated reliably with ICP-OES, the TiC content was calculated by assuming all Ti bonded, likely overestimating its content.

Table 3 | Chemical composition of AA7075 and commercial 7075 (as reference) determined by ICP-OES (1 measurement). All values are in weight percent

	Zn	Mg	Cu	Ti	Si	Cr	TiC	Al
7075NT powder	13.25	3.56	1.60	1.16	0.10	<0.01	1.45	Bal.
As-printed	8.77	2.63	1.67	1.21	0.09	<0.01	1.51	Bal.
Commercial 7075 (composition range)	5.70 (5.6- 6.1)	2.55 (2.1- 2.6)	1.50 (1.2- 1.6)	0.30	0.07	0.20	N/A	Bal.

4.3 Additive manufacturing

The 7075NT powder was additively manufactured into bulk samples using a Renishaw (United Kingdom) AM400 L-PBF machine. The machine is equipped with a Nd: YAG laser ($\lambda=1064$ nm) with a maximum power of 400 W, a gaussian power distribution, and a nominal beam spot size of 70 μm . The laser operates in a pseudo-pulse mode, in which the laser illuminates an area for a set exposure time (t) before jumping to the next spot. The laser turns off in between two exposure spots. The distance between two points, in the direction of motion of the laser, is denoted as point distance (pd). The apparent scanning speed ($\bar{v}$) of the laser is given by $\bar{v} = \frac{\text{pd}}{t}$. All printing was done after calibration of the laser power via a power meter (Ophir Optonics, USA) at a set power of 150 W. The measured power was 148.9 W. Due to the small deviation between the set power and the actual power, the laser power mentioned herein will be the set power for simplicity. All 7075NT samples were printed on commercially pure Al build plate, purchased from Renishaw.

All samples were printed with a double scanning strategy: each layer of freshly coated powder was subjected to a primary scan and then a secondary scan. The primary scan used a “chessboard” pattern, in which the entire designed area is divided into 4 mm squares. The laser scans within a square before moving to the next. Adjacent squares have scanning vectors perpendicular to each other. The secondary scan uses a “meander” pattern. Between each recoating layer a rotation of 67 degrees was implemented. The sample geometry and laser scanning pattern file were prepared using the commercial software Materialise Magics. The oxygen level in the chamber was maintained below 150 ppm during printing. Printing parameters are tabulated below in Table 4.

Table 4 | AA7075 printing parameters

	Power, P (W)	Exposure time, t (μ s)	Point distance, pd (μ m)	Equivalent speed, $\bar{v}$ (mm/s)	Layer thickness, l (μ m)	Hatch distance, h (μ m)
1 st scan	170	50	30	600	30	50
2 nd scan	300	25	30	1200	N/A	60

4.3.1 *Post processing of the as print AA7075 samples*

The as-printed (AP) AA7075 samples were removed from the build plate and sliced into 1.5 mm sheets using electrical discharge machining (EDM). The AP sheets were subjected to a two-step heat treatment, first a solutionization step at 470 °C for 1 hour in air using a muffle furnace before quenching to room temperature in water, followed by an artificial aging process (named T6 herein) at 120 °C for 16 hours.

To eliminate porosity, additional as-print AA7075 samples were subjected to a hot isostatic pressing (HIP) treatment. The HIP service was provided by American Isostatic Presses, Inc. The treatment was carried out at 470 °C in 200 MPa of Ar atmosphere for 90 minutes before water quenching.

4.3.2 *Mechanical testing*

Tensile testing specimens with a gauge section of 1.3 mm $\times$ 1.5 mm $\times$ 4 mm (thickness $\times$ width $\times$ length) were prepared from the AA7075 sample sheets by EDM. Specimens were polished on all sides using 600 grit SiC papers to remove the affected layer due to EDM. Tensile tests were carried out using an Instron 5960 Universal Testing Machine. The strain measurement was taken

by the machine-equipped non-contact Standard Video Extensometer (SVE). All tensile tests were performed at a constant strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ at ambient conditions.

4.3.3 *Microstructure characterization*

All metallographic specimens were polished with progressively finer SiC papers (600-1200grit) and then diamond slurries (3, 1, 0.25, and 0.05 μm). SEM characterization of the powders was performed on a Zeiss Supra 40VP SEM at 15 keV. SEM micrographs were also taken to evaluate the porosity fraction, as a comparison to the results acquired by micro-CT.

A FEI NOVA nanoSEM 230 was used for microstructural characterization. Accelerating voltages ranging between 5-20 keV were used, with working distances between 4-10 mm. EDS maps were collected with a WD of 5-10 mm and current of $\sim 4\text{-}6 \text{ nA}$. EBSD characterization was carried out using a Bruker eFlash detector, a voltage of 20 keV, current of 3-12 nA, WD of $\sim 20 \text{ mm}$, and step sizes ranging from 200 nm to 4 μm , depending on magnification. Dwell times between 5-20 ms were used. EBSD samples were polished following the same metallographic procedure described above but were further etched with Keller's reagent for $\sim 3\text{-}10$ seconds. Data was processed using Bruker's Esprit 2.5 software.

4.2.6 Synchrotron X-ray Diffraction (SXRD)

All samples were analyzed during in-situ tensile testing at beamline ID3A at Cornell High Energy Synchrotron Source (CHESS). The beam energy was set at 51.996keV with a beam size of $500 \mu\text{m} \times 500 \mu\text{m}$. Diffraction patterns were collected on two Dexela 2923 detectors, each with size $290.8 \times 229.8 \text{ mm}$ and pixel sizes of $74.8 \times 74.8 \mu\text{m}^2$. The in-situ mechanical tests were performed with a RAMS2 machine, at a constant strain rate of 3.5×10^{-5} . A high temperature furnace equipped with Ar flow was also attached to the RAMS2 to obtain high temperature in-situ

monitoring. Pin-loaded dog-bones with small gauge sections ($1.6\text{ mm} \times 2\text{ mm}$, $h \times w$) were used to accommodate the geometrical restrictions of the tensile test set-up. Two detector-to-sample distances were used, respectively at 56cm and 120cm—the latter roughly doubled the resolution of the XRD peaks, thus allowing for a more accurate peak fitting, especially for precipitates indexing. All XRD patterns were calibrated using a reference CeO_2 powder standard (ASTM 674b).

4.3.4 *Transmission electron microscopy*

All the transmission electron microscopy (TEM) samples, including pristine AP, HIP and HIP+T6 conditions and their deformed counterparts for post-mortem investigation of deformation behavior, were prepared using the FIB lift-out method in an FEI Quanta 3D microscope equipped with an OmniProbe. A final polish at 5 kV and 48 pA was used to minimize the ion beam damage to the TEM sample. Ion beam damage on the TEM samples was further cleaned in a Fischione Nanomill™ Model 1040 system. The atomic structures of pristine and deformed Al alloy and the elemental distribution of the precipitates were characterized using a JEOL JEM-ARM300F Grand ARM TEM with double Cs correctors operated at 300kV. A probe current of 35 pA and inner and outer collection angles of 106 and 180 mrad were used for high angle annular dark field (HAADF) imaging. Dislocations in deformed samples were analyzed under convergent beam electron diffraction (CBED) mode. Bright-field scanning transmission electron microscopy (BF-STEM) images for dislocation analysis were captured at a camera length of 40 cm, with a dwell time of 4-6 s. A convergence semi-angle of 1 mrad using a 10 μm condenser (C4) was used to separate the diffraction disc in the CBED pattern, isolating the diffraction signal. For dislocation-morphology characterization, samples were tilted to a standard two-beam condition by exciting the g beam with an excitation error near zero, and a suitable objective aperture was inserted to ensure that only the

transmission beam to be detected on the BF detector. Atomic-resolution energy dispersive X-ray spectroscopy (EDS) chemical maps were acquired with a dual detectors system inserted in the large-gap objective pole piece. The EDS data processing was performed using JEOL Analysis Station software.

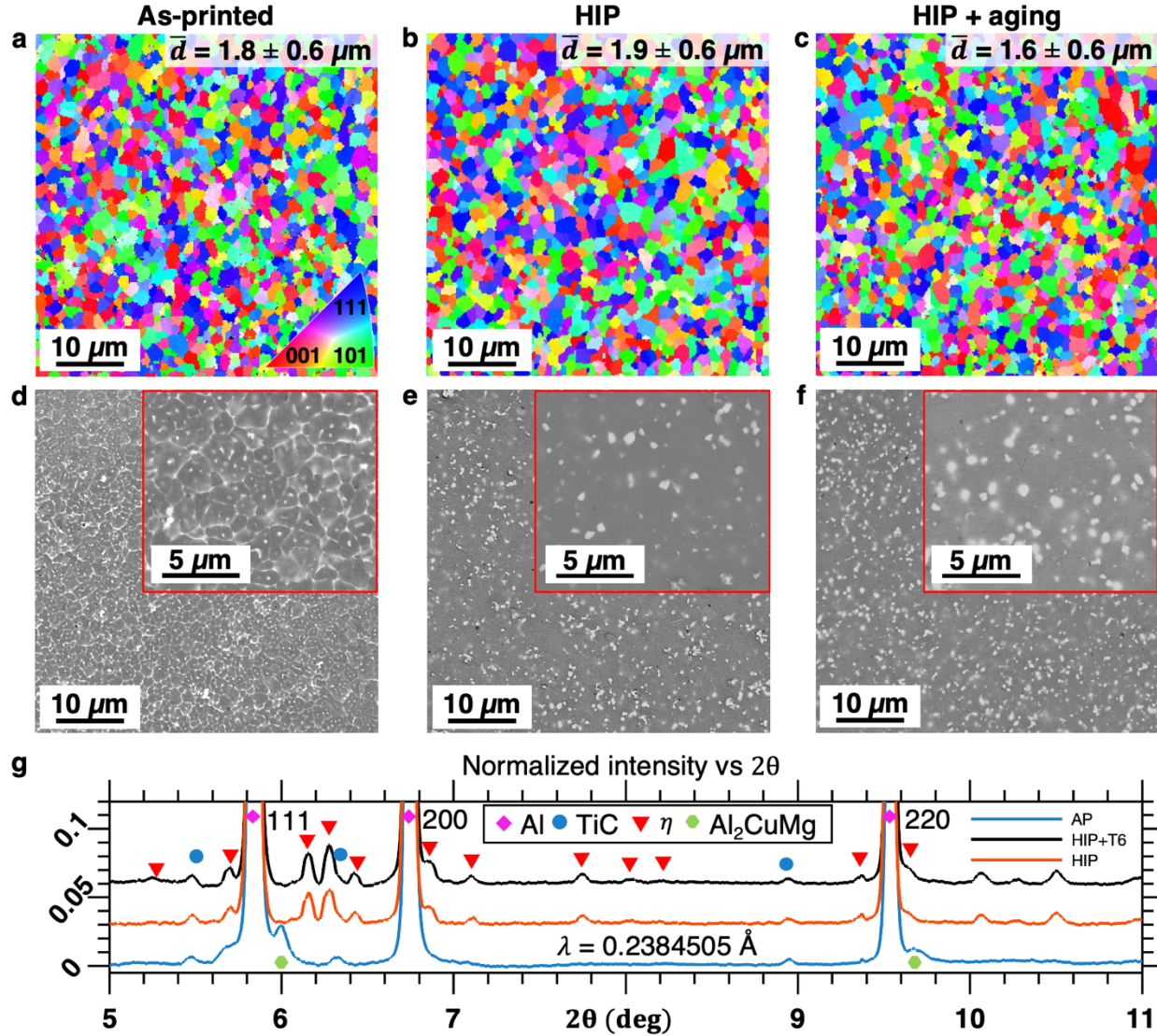


Figure 23 | Microstructure characterization of as-printed and heat-treated samples. a-c electron backscattered diffraction (EBSD) map of the three Al samples. Fine equiaxed grains are observed for all three, suggesting good grain boundary (GB) thermal stability. **d-f.** Scanning electron microscope (SEM) images showing larger precipitate decorating the GBs. HIP and H6 samples appear similar at this scale **g.** X-ray diffraction (XRD) spectra comparing the three

samples—more MgZn_2 forms after heat treatments and does not dissolve during aging. TiC (blue dots) remain unaffected.

4.4 Results

Following successful printing of the 7xxx series alloy, two heat treatments were applied: a HIP procedure, followed by an age hardening (T6) treatment to further optimize mechanical properties (see methods for specific parameters). In this work, data for all three samples are presented, with emphasis on the aged sample (herein referred to as “H6” or “aged”,) given its exceptional combination of strength and ductility. Characterization of the AP and HIP samples-- the precursors to H6-- serve as the basis to understand the properties reported for H6.

4.4.1 Microstructure

Figure 23 displays the microstructure of the three samples. EBSD maps show near identical distributions across the three samples, within error, with grain sizes of $1.8 \pm 0.6 \mu\text{m}$, $1.9 \pm 0.6 \mu\text{m}$, and $1.6 \pm 0.6 \mu\text{m}$, for AP, HIP, and H6 respectively (Figure 23a-c). While the average grain size remains nearly unchanged despite the high temperature heat treatments, subfigure d-f show significant changes in the chemical redistribution. In the AP state, large quantities of solute atoms decorate the GBs, as seen in the insert of Figure 23d. Many particles are also found on the inside of the grains, distributed in a stochastic manner. After HIP, the solute redistributes across the matrix, depleting the GBs of a significant amount of its starting quantity, but leaving some large particles behind, mainly at triple points and along grain boundaries.

Figure 23 d-f compares the evolution of solute segregation and precipitation. In the AP state, large quantities of solute areas are found, with strong segregation at both grain boundaries (GBs) and at grain interiors. Following HIP, despite no appreciable changes in grain size, the

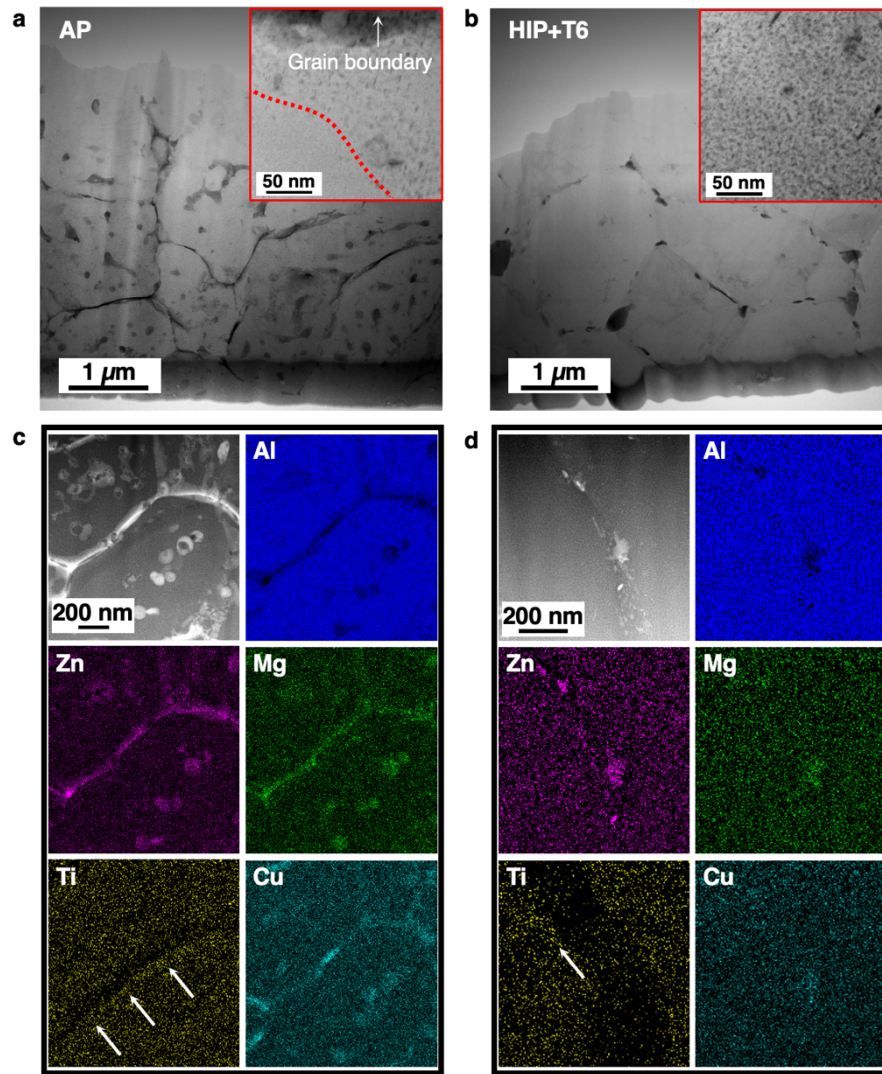


Figure 24 | Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) maps of AP and aged samples. a TEM images of AP sample showing solute segregation around grain boundaries (GBs). Insert shows higher magnification TEM near a GB, with nanoscale precipitation visible. **b** Same as **a**, for H6. Finer and more homogeneous nanoprecipitates are observed. **c** Energy dispersive spectroscopy (EDS) maps of the main solute elements in the alloy. TiC clustered at boundaries with MgZn_2 is pointed out by white arrows. **d** EDS for H6, finer precipitation is observed on boundaries.

chemical landscape shows significant solutionization, with large particles left behind at GBs and at triple points. An XRD spectrum is displayed in Figure 23g, highlighting the change in

chemical composition taking place during heat treatments-- the resulting spectra for HIP and H6 are similar, with only two phases present (MgZn_2 and TiC). Some MgZn_2 is also present in AP (blue curve), however its signal is much weaker, indicating a lower volume fraction. The amount of TiC remains stable across the three conditions (blue circles). We also note that AP has two strong peaks indexed as AlCu_2Mg , suggesting this compound forms at grain boundaries during solidification. At this length-scale, HIP and H6 appear almost identical in nature, however clear differences should be seen at the nanoscale level, since the T6 (age hardening) process is designed to nucleate nano-sized metastable strengthening phases (η').

Higher magnification TEM images are displayed in Figure 24 for AP and H6. Fine, dense precipitation of spherical clusters as well as more needle-shaped strengthening phases are visible. This is evident in the insert of b and is present throughout the sample. In contrast, AP shows solute-rich regions throughout the sample, but only displays signs of needle-shaped phases near GBs. Figure 24c, d show energy dispersive spectroscopy (EDS) maps of the two samples, identifying the larger GB phases as being Mg, Zn, and Cu rich. In H6, finer intermediate precipitation on the order of a few tens of nanometers is observed along the GBs. Some areas of slightly higher Ti concentration near GBs (white arrows, 24c) are found, suggesting that TiC particles preferentially segregate at boundaries. This observation supports the GB pinning effect of TiC mentioned earlier. Figure 24 does not include results for HIP because its grain structure at the scale of the lower magnification image is very similar to b. Both heat-treated samples have grains surrounded by large MgZn_2 precipitates on the order of a few hundred nanometers, as well as smaller (tens of nanometers) ones along GBs. At the nanoscale, HIP resembles H6, with the only difference being the lack of age-hardened particles.

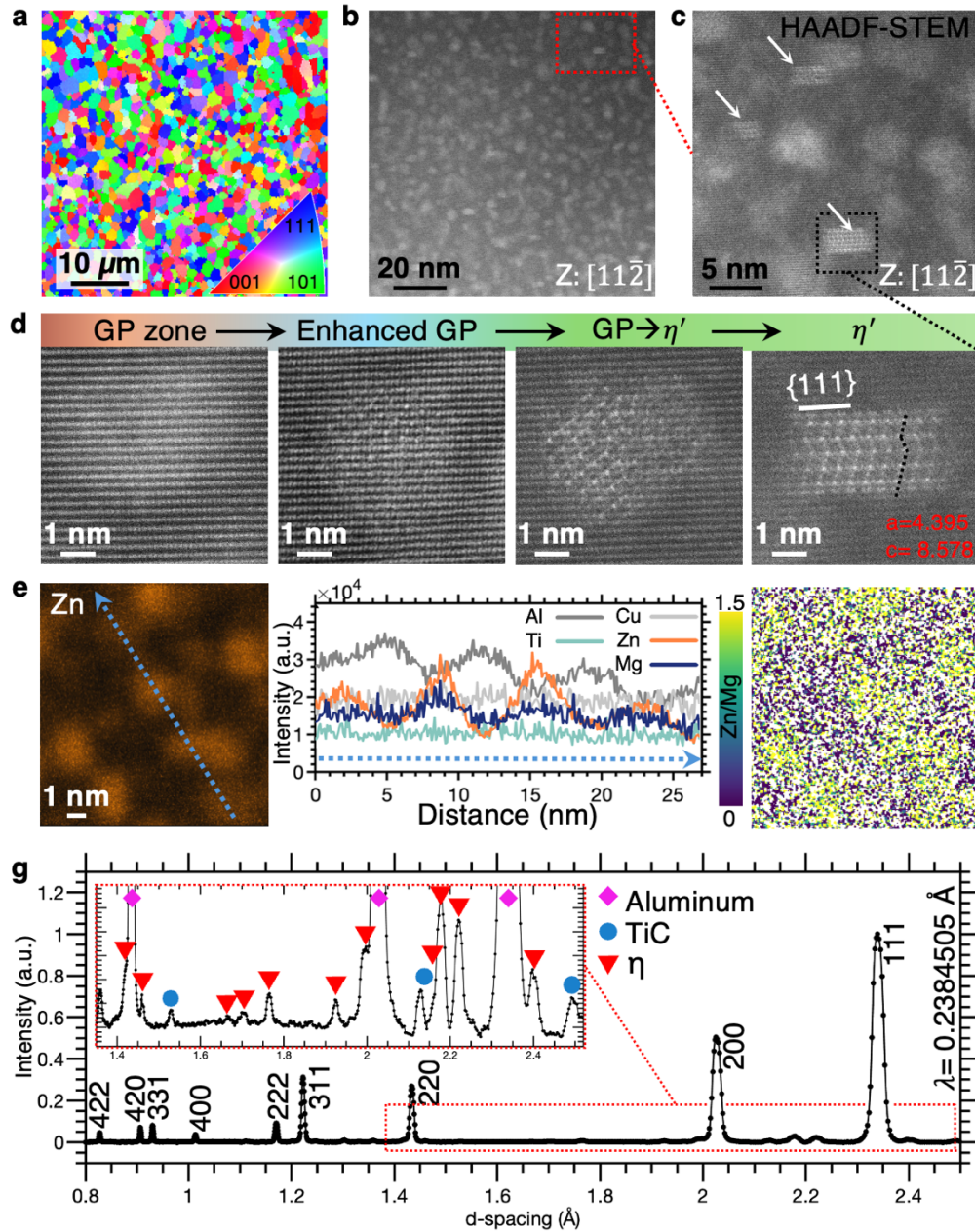


Figure 25 | Hierarchical microstructure of an additively manufactured 7xxx series aluminum alloy post heat-treatment. **a** Electron backscattered diffraction (EBSD) map showing $\sim 1.6 \pm 0.6$ μm grains and no strong texture. **b** High angle annular dark field transmission electron microscopy (HAADF-TEM) revealing well-dispersed nanoscale precipitates in H6. **c** Higher magnification of region in **b**. Arrows point at η' precipitate. **d** Four different precipitate types found in H6. **e** Energy dispersive spectroscopy (EDS) map of precipitates in **d** showing high Zinc regions and various

chemical ratios (Zn/Mg). Blue arrow shows location of adjacent line scan. **g** Synchrotron x-ray diffraction (SXRD) pattern showing main phases after heat treatment; inset highlights indexed precipitate peaks.

A representative scanning transmission electron microscopy (STEM) map of H6 is presented in Figure 25b, with its fast Fourier transform (FFT) as an insert. The image is collected on a high angle annular dark field (HAADF) detector, used to visualize changes in atomic number (Z) contrast; the lighter areas are nanoscale precipitates high in Zinc and Magnesium content, which mostly formed during the T6 treatment. Nano precipitates with different shapes (elongated, as opposed to disk-shaped—white arrows in 25c) are found throughout. The average size of the nanoscale precipitates is calculated to be 2.055 ± 0.504 nm (assuming spherical geometry) and their volume fraction ($\sim 1.245\%$), as calculated from STEM images (over 200 particles were counted for statistical purposes).

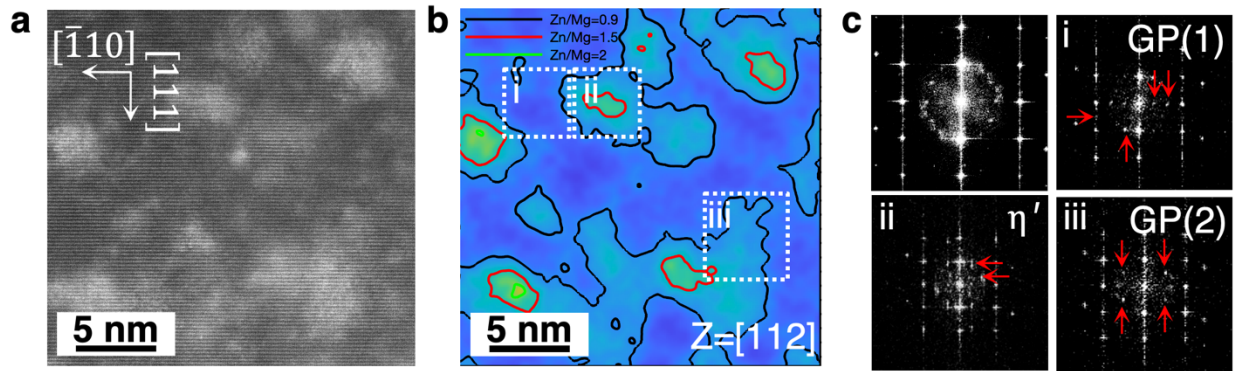


Figure 26 | Nanoscale chemical heterogeneity EDS mapping. **a** Dark field transmission electron microscopy (BF-TEM) showing another region on H6, precipitate rich regions are present. **b** Atomic percentage ratio Mg/Zn displayed from energy dispersive spectroscopy (EDS) of **a** Fast Fourier Transforms (FFTs) from image **a**, red arrows point at the typical signatures of the respective phases. Areas with lower Zn/Mg content appear to be Guinier-Preston (GP)1 zones, with spots at $1/3, 2/3 \{220\}$. Regions with the highest ratio show spots at $1/3, 2/3 \{220\}$ with light streaking towards the $\{111\}$, indicative of metastable η' . Intermediate Zn/Mg ratios show signs of GP2 zones, namely spots at $1/2 \{311\}$

Identifying the nano precipitates' phase and composition is of interest for a thorough prediction of their strengthening contribution. Figure 25d displays examples of different types of precipitates present in the H6 sample. From left to right, we see coherent, GP-zone like clusters, followed by transition structures that eventually nucleate the η' phase. 25e shows an EDS map highlighting areas with higher Zinc content. A line scan with the elements present in the system is

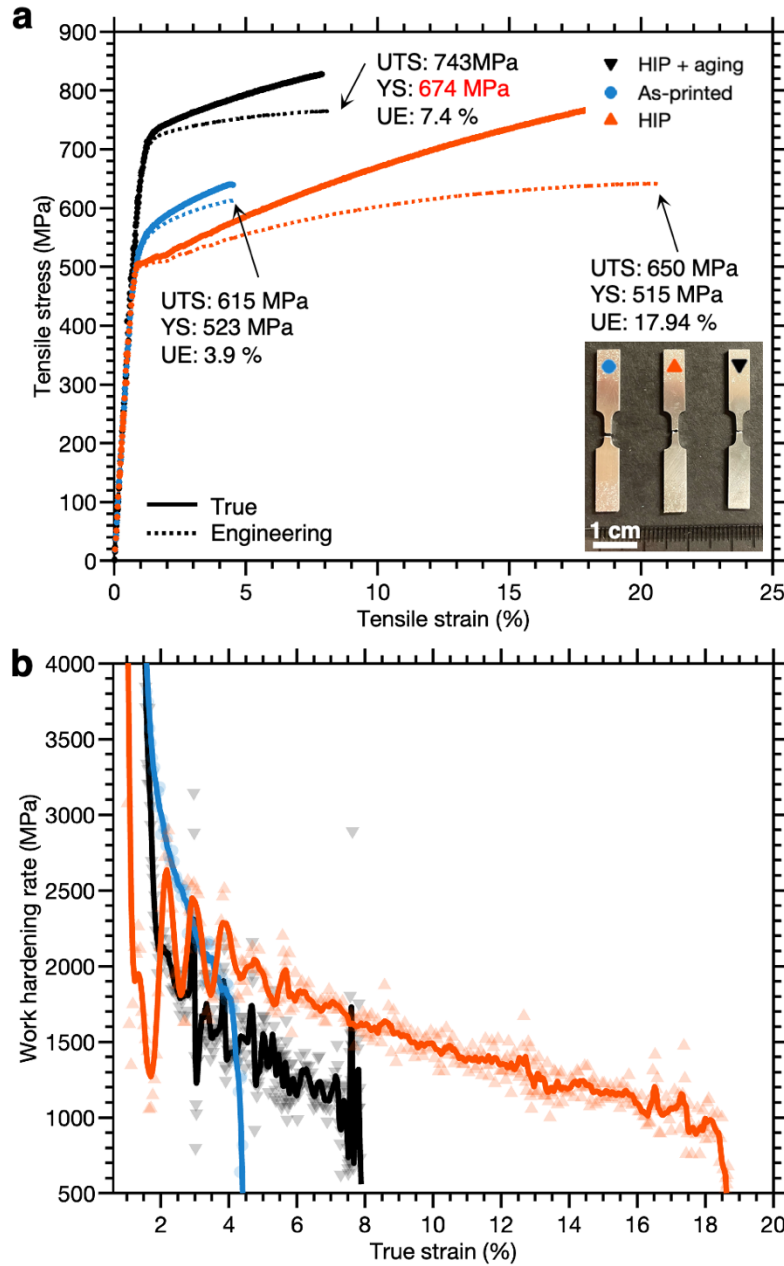


Figure 27 | Tensile properties. **a** Representative tensile property for the additively manufactured (AM) AA7075 samples in this work **b** Normalized work hardening plot for the three samples in **a**. The hot isostatic pressure (HIP) sample shows strong fluctuations right after yielding, likely due to interplay between matrix and large precipitates--this is also visible in the stress-strain curve in **a**.

obtained and shows the different chemical composition of various precipitates. A Zn/Mg atomic ratio map created by EDS signal is also provided, showing regions with higher ratios

relative to the surroundings. Higher Zn/Mg ratios are associated with different stages of η' formation. Overall, the sample shows a wide range of chemical compositions on the nanoscale.

A second example displaying the different phases present and their relation to chemical composition is shown in Figure 26. Like Figure 25, the Zn/Mg ratio is displayed in Figure 26b from the TEM image in a. Here, averaging was carried out to better visualize the composition. The contour lines delineate different concentration ratios, highlighting the heterogeneity of the sample at this scale. FFT patterns of the regions inside the white squares are shown in Figure 26c. Each FFT reveals signatures of different strengthening phases (red arrows): lower Zn/Mg ratios are associated with GP1 zones, with distinguishing diffraction spots appearing at $1/3$, $2/3$ $\{220\}$. Slightly higher ratios show clear reflections at $1/2$ $\{311\}$, associated in the literature with GP2 zones. Lastly, higher Zn/Mg ratios tend to correlate with the formation of η' , judging by presence of streaked spots in the direction of $\{111\}$. The complete FFT of Figure 26a is shown on the top left of Fig. 26c. The purpose of these data is to highlight the prevalence of chemical inhomogeneity at small scales, and to show that the abundance of solute atoms (as is the case for our AM alloys, see methods) incentivizes the formation of many metastable precursors to the major strengthening phases (η').

FFT indexing was used to visualize different phases because synchrotron x-ray diffraction (SXRd) could not detect GP zones, due in part to their low signal and peak overlap with the matrix signal. The SXRd intensity spectrum in Figure 25g shows all detectable phases in the H6 sample, color coded according to the legend. Notice that other than TiC, all other present peaks correspond to the η phase, specifically with a hexagonal crystal structure with $a=5.205$ Å and $c=8.501$ Å.

4.4.2 Tensile properties

The complex microstructure reported confers excellent mechanical properties to the materials, as seen in Figure 27-28. Representative stress-strain curves are shown in Fig. 27a; first, we note that the strength of both the AP and HIP samples is high relative to conventional Al7xxx series alloys. However, the AP sample suffers from low ductility, likely due to premature failure induced by residual stresses and/or sporadically placed porosity. After HIP, both of those issues are resolved—yield strength does not change significantly (slightly lower than AP), but its uniform elongation (UE) increase more than four-fold (3.9 % to 17.94 %). Its work hardening behavior should also be noted, as the sample reaches an impressive engineering ultimate tensile strength of ~650 MPa (~770 MPa true stress).

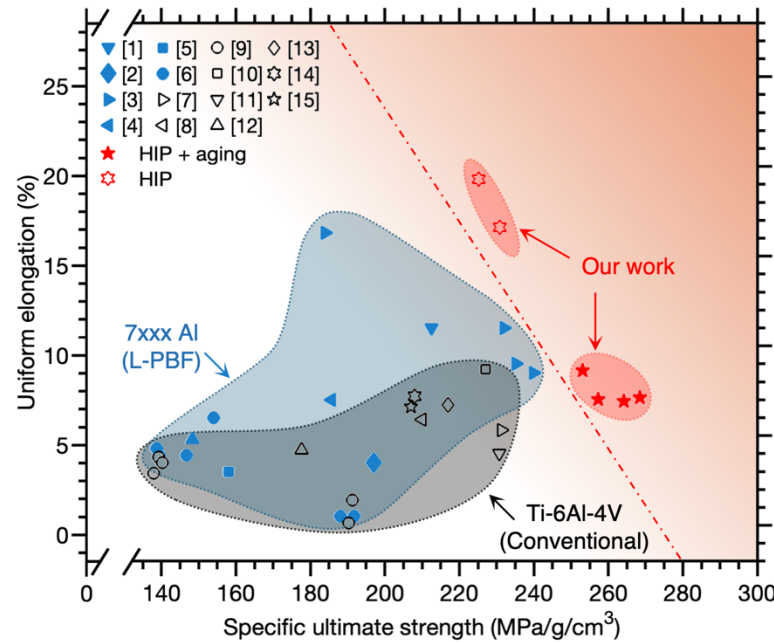


Figure 28 | Mechanical properties comparison of AM AA7075 samples to the available literature. Refs: [16, 20, 36, 60, 161, 38, 162, 163, 164, 165, 163, 49].

The T6 aging treatment optimized ductility and strength, resulting in the highest reported specific ultimate tensile strength (UTS) to date, with the best sample reaching 764 MPa (827 MPa true stress). The Ashbey diagram in Figure 28 compares our work to the available literature for specific ultimate tensile strength (SUTS), useful when comparing dissimilar systems. The black data points compare our results to the strength and ductility of conventional Ti-6Al-4V (Ti64), highlighting the new Al 7xxx alloy's ability to significantly surpass a system known for its high strength and low density. Figure 27b calculates the work hardening rate for the three samples shown in Fig. 27a. The AP sample starts with the highest value, likely because of the denser network of dislocations in the sample, and the large quantities of solute agglomeration that encapsulates each grain—these factors, likely coupled with some left-over porosity and residual stresses, led to premature failure right at 4% true strain. After HIP, the hardening rate is much lower in the early stages of deformation. As yielding initiates, large oscillations are measured, akin to the Lüder band effect found in some Al-Mg alloys and in low-carbon steels [16]. The hardening rate increases rapidly, reaching a peak at ~3% strain, and slowly decays until failure at ~18%. Lastly, the aged sample initially has a hardening rate between the other two. The initial higher rate is likely related to the much higher concentration of nanoscale precipitates and chemical local inhomogeneity resulting from aging, alongside a dislocation density slightly higher than HIP, but lower than AP. The rate then decays steadily, like in HIP.

Unraveling of the mechanisms responsible for these mechanical responses require consideration of all available strengthening mechanisms. All parameters used for yield strength (YS) prediction will be discussed in the next section.

4.4.3 Strengthening mechanisms

To identify the nature of the exceptional mechanical properties of this material four categories of strengthening mechanisms are explored, namely GB, solid solution (SS), dislocation, and precipitation strengthening.

4.4.3.1 Grain boundary strengthening

The GB mechanism is calculated according to the Hall-Petch relationship:

$$\sigma_{GB} = \sigma_0 + \frac{k_y}{\sqrt{d}} \quad (1)$$

where d is the mean grain diameter of the alloy, σ_0 is the friction stress of the matrix (aluminum), and $k_y = 0.12 \frac{\text{MPa}}{\sqrt{\text{m}}}$ is the Hall-Petch slope for AA7075 [38]. From Figure 23a-c, the average grain sizes yield GB strengthening contributions of 89.4 MPa, 87.1 MPa, and 94.9 MPa, respectively for AP, HIP, and H6. Even though this mechanism is not the largest contributor to the alloys' yield strengths, its share is a result of the TiC nanoparticles, which refine the microstructure.

4.4.3.2 Solid solution strengthening

To account for solid solution strengthening, solute concentrations were measured (see methods) to estimate the strengthening and calculated according to the formula [82]:

$$\Delta\sigma_{SS} = 2.9 [C]_{\text{Zn}}^{\text{wt}\%} + 18.6 [C]_{\text{Mg}}^{\text{wt}\%} + 13.8 [C]_{\text{Cu}}^{\text{wt}\%} \quad (2)$$

Here C represents the wt.% concentration of the respective solute element. It is assumed that all samples, regardless of heat treatment, have the same chemical composition: 8.77 wt%_{Zn}, 2.63 wt%_{Mg}, and 3.67 wt%_{Cu}, obtaining a contribution of ~97.4 MPa for SS strengthening. Because heat treatments

significantly changed the percentage of solute atoms in solid solution (through formation of precipitates and clusters) the calculation provided above is an upper bound obtained on the assumption that all solute atoms contributed to SS strengthening. This assumption inherently overestimates the contribution of the mechanisms, especially for AP, which holds most of its solute atoms along GBs.

4.4.3.3 Dislocation strengthening

The pre-existing dislocations prior to tensile testing has a non-negligible impact on the mechanical properties, as well as the precipitation behavior of the sample [85]. Dislocation strengthening is calculated according to the Taylor equation:

$$\Delta\sigma_{\text{dis}} = M\alpha Gb\sqrt{\rho} \quad (3)$$

where M is the mean orientation factor, taken to be ~3.06 for FCC aluminum, b is the magnitude of the burgers vector (0.286 nm), α is a dimensionless constant equal to 0.2, G is the shear modulus of the matrix (26.9 GPa for AA7075), and ρ is the dislocation density. Dislocation density can be approximated from a peak broadening analysis using a modified Williamson-Hall (m-WH) plot. To calculate the effect, Synchrotron x-ray diffraction (SXR) was used to track multiple diffraction reflections. Equation 11 is then employed:

$$\Delta K^2 = \left(\frac{0.9}{D}\right)^2 + \frac{\pi A^2 b^2 \rho}{2} (K^2 \bar{C}) + O(K^2 \bar{C})^2 \quad (11)$$

Here, ΔK represents the width of the peaks, D is the crystallite size, A is a coefficient related to the outer cutoff radius of dislocations (taken to be approximately 1.4 in this work), ρ is dislocation density, b is the burgers' vector of aluminum (0.286 nm), and $\bar{C}$ is the average contrast factor of the system, which is dependent on the fraction of screw and edge dislocations and their dependence on hkl orientations, as well as the elastic constants of the matrix [94,121,128,131]. As reported in Figure 29 for H6, the linear fits of ΔK^2 vs $K^2\bar{C}$ yield initial dislocation densities for AP, HIP, and H6 of 3.359 , 1.632 , and $2.078 \times 10^{14} \text{ m}^{-2}$ respectively.

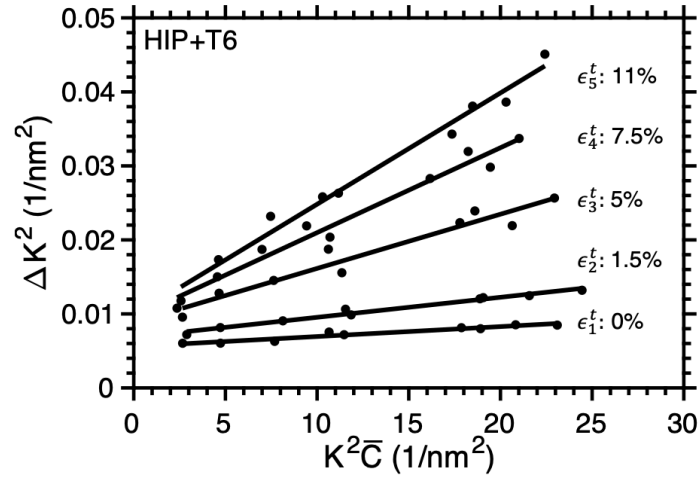


Figure 29 | m-WH plot evolution as a function of applied strain in H6. Increasing slope is related to dislocation density accumulation.

Using Equation 3, the dislocation density contributions to strengthening are 86 MPa, 60 MPa, and 68 MPa. This higher initial dislocation density in AP is expected because of the extremely rapid cooling experienced by the alloy during printing, alongside the inevitable thermal cycling that occurs during L-PBF; fast solidification and thermal cycling are known to introduce dislocations and vacancies into the system. Subsequent heat treatments released some stresses and allowed dislocations to migrate and annihilate, resulting in a lower density. However, the HIP+T6

had a slightly larger value than HIP, likely a result of the introduction of a dense network of η' precipitates during age hardening, which hindered dislocation motion and prevented their mutual annihilation. The presence of dislocations despite the long heat treatment is consistent with the literature [81]. Figure 29 also shows the dislocation density evolution (slope) during in-situ SXRD loading for H6—an upward trend suggesting dislocation accumulation is observed. This will be discussed more in depth in the next section.

4.4.3.4 Precipitation strengthening

The 7xxx series (Al-Mg-Zn-Cu) generate a variety of phases during manufacturing, of which the η' phases are responsible for most of the strengthening. Precipitates can be either coherent, semi coherent, or incoherent with the matrix—leading to two potential active mechanisms. Equations 4-7 outline the individual factors that play into the process; the main contributors are precipitate volume fraction, size, lattice spacing misfit, and elastic properties of the shearable particles.

The multiple mechanisms are always competing; to determine which equations apply, a strengthening map can be constructed by employing all 4-7 simultaneously and defining that Orowan looping is the active mechanism if $\Delta\sigma_{\text{orowan}} < \Delta\sigma_{\text{cs}} + \Delta\sigma_{\text{ms}}$. In other words, the mechanism that produces the lower strengthening effect is the active one [81].

$$\Delta\sigma_{\text{orowan}} = M \frac{0.4Gb \ln\left(\frac{2\bar{r}}{b}\right)}{\pi\sqrt{1-\nu}\lambda_p}; \bar{r} = \sqrt{\frac{2}{3}}r \quad (4)$$

$$\Delta\sigma_{\text{cs}} = M\alpha_{\epsilon}(G\epsilon_c)^{\frac{3}{2}}\left(\frac{rf}{0.5Gb}\right)^{\frac{1}{2}} \quad (5)$$

$$\Delta\sigma_{\text{ms}} = M0.0055(\Delta G)^{\frac{3}{2}}\left(\frac{2f}{G}\right)^{\frac{1}{2}}\left(\frac{r}{b}\right)^{\frac{3m}{2}-1} \quad (6)$$

$$\Delta\sigma_{os} = M0.81 \frac{\gamma_{apb}}{2b} \left(\frac{3\pi f}{8} \right)^{\frac{1}{2}} \quad (7)$$

Evaluation of the equations is shown in Figure 26c, where color represents the strengthening effect by Orowan looping as a function of precipitate size and precipitate volume fraction. The red star indicates the values measured for the H6 sample, where the high nanoscale precipitate volume fraction of ~1.25%, alongside a mean precipitate radius of 2.055 ± 0.504 nm contributed almost 400 MPa to the H6 yield strength. The active mechanism was found to be Orowan looping, implying that the contribution to strength is assumed to only be dependent on the size distribution of the precipitates, regardless of their chemistry. The exact values obtained for the mechanisms are reported in Table 5. The variables used in equations (4-7) can be found in the literature [81].

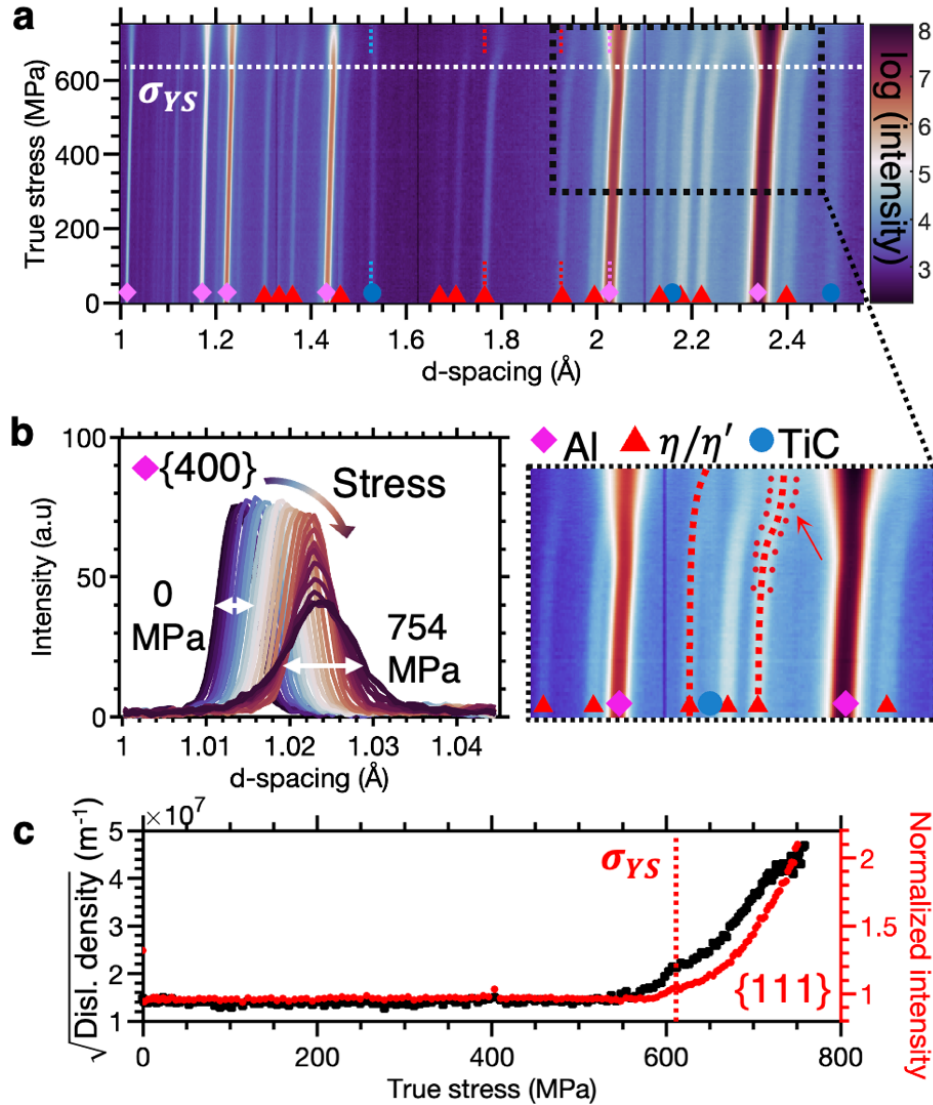
Table 5 | AA7075 printing parameters

	Mechanism	Orowan	Coherent	Misfit	Order
$\Delta\sigma_{YS}$ (MPa)	388.5	1427.5	195.3	105.2	$\Delta\sigma_{YS}$ (MPa)

4.4.4 In-situ synchrotron X-ray diffraction (SXRd)

The deformation mechanics at play can be observed in real time via SXRd. All samples were subjected to an in-situ tensile test while high brilliance and energy x-rays were used to probe

their internal deformation in real time. A schematic of the in-situ transmission geometry is shown



in Figure 5.

Figure 30 | In-situ synchrotron X-ray Diffraction (SXRD) of H6 aged sample. a In-situ SRXD intensity spectra (color) plotted as a function of applied true stress (y-axis). Colored symbols index respective precipitates and matrix peaks. A magnified region in the insert highlights lattice deviation and broadening in **b**. **b** Regular SXRD spectra plotted as a function of stress for the matrix {400} planes. White arrows show broadening increase at 0 MPa and just before fracture. **c** Dislocation density evolution and {111} texture change along the loading direction (LD). Dotted red line represents macroscopic yield strength (YS). Notice the slight increase and subsequent temporary plateau in both curves.

4.4.4.1 Dislocation density and texture evolution

Figure 30 displays SXR D results for the H6 sample. In 30a multiple XRD spectra are plotted in sequence, where color indicates diffraction signal intensity. Each row represents an XRD spectrum at a particular macroscopic stress level (y-axis). We first address the broadening effect of plastic deformation in Fig. 30a-b; here, both the matrix and precipitate peaks broaden after yielding (dotted white line). The insert shows a magnified region of the map that highlights the broadening and position changes. As discussed above, broadening is associated with defect accumulation, which is corroborated by the width increase near and past macroscopic yielding. The same $\{400\}$ data found at $\sim 1\text{\AA}$ in the map is replotted as a typical intensity vs Bragg angle in Fig. 30b. The white arrows highlight to the dramatic increase of full width half max (FWHM) from the zero-stress state to just before fracture.

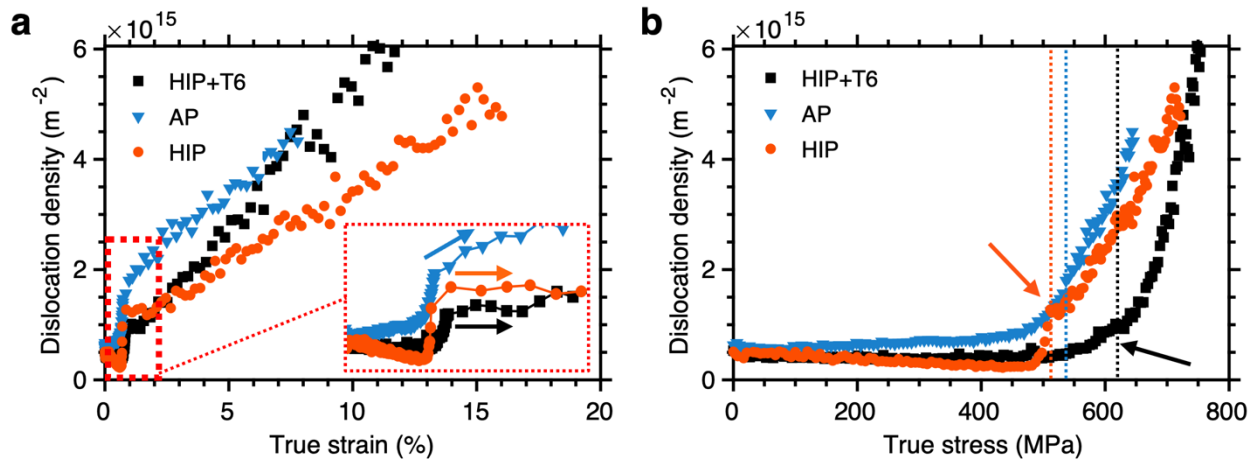


Figure 31 | Dislocation density evolution comparison. **a** Dislocation density evolution as a function of true strain and true stress **b** Dotted lines represent color-coded values for yield strength (YS). The insert in **a** and arrows in **b** show the plateau behavior associated with the heat-treated samples.

All matrix reflections were tracked and analyzed using the procedure to plot the dislocation density as a function of macroscopic stress along the loading direction (Figure 30c, black line). Two main features are highlighted: a slight, but rapid increase right before macroscopic yield

strength (red dotted line), which indicates that some early plastic activity initiates at the microscopic level. Followed by a short plateau right after YS, which resumes soon after and eventually behaves more linearly with increasing stress. We point out that the y-axis is the square root of dislocation density, chosen to highlight the relationship in equation 3.

On the same plot, relative intensity of the $\{111\}$ family shows a similar trend: a slight increase right before YS, followed by a slower rate of change during the dislocation plateau. The initial $\{111\}$ intensity change signifies slight grain rotation towards the loading direction because of plastic activity, consistent with the concurrent increase in dislocation density.

Figure 31a-b displays the dislocation evolution for all three samples as a function of true strain and true stress, respectively. Here AP shows a rather monotonically increasing behavior, with a modest increase as yield is approached, followed by a steady defect accumulation up to fracture. In contrast, HIP appears to have an initial slightly negative trend during the elastic regime, implying a reduction in defect density despite the applied tensile load. Beyond this initial trend, HIP and H6 display similar trends, with increases right before YS—steeper in HIP—followed by a plateau. Both samples then begin increasing again, eventually following a linear relationship with stress. The rates of dislocation accumulation are higher in H6, followed by AP and HIP, their final values scale with their respective UTS values.

Because the heat-treated samples continue to both strengthen and elongate macroscopically while dislocation activity in the matrix momentarily stagnates during the post-YS plateaus, a deeper analysis of the interplay between matrix and precipitates during deformation is necessary. Lattice strain and load partitioning analyses will shed light on these mechanisms in section 4.3.4.2.

4.4.4.2 Lattice strain and load partitioning

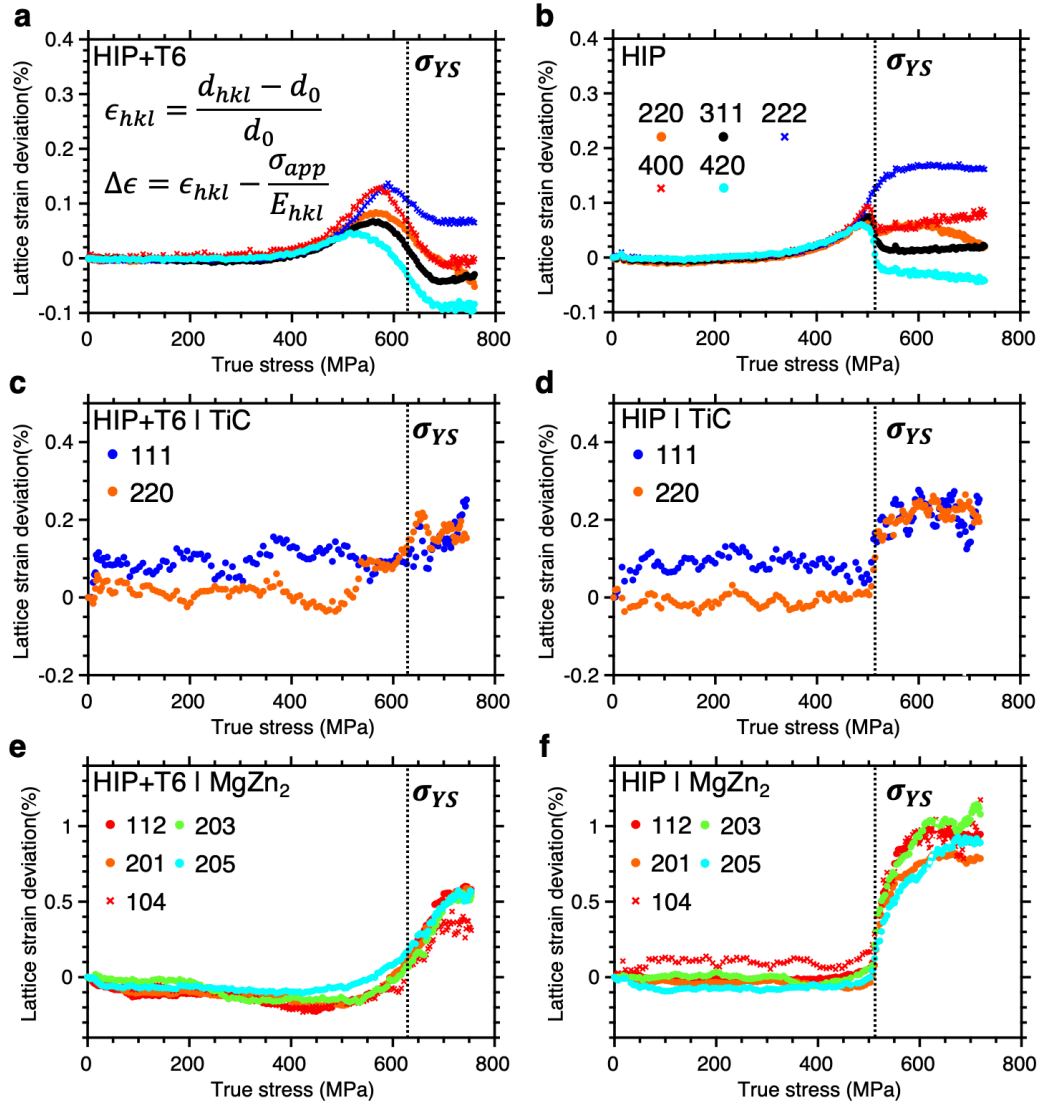


Figure 32 | Lattice strain deviation along loading direction (LD) in HIP and H6 for multiple matrix reflection families, TiC, and η precipitates. a-b Lattice strain deviation for H6 and HIP as a function of true stress. A hump behavior is observed in both, with {111} carrying more load in HIP. **c-d** equivalent to a-b, for TiC. An upward trend (clearer for HIP) is seen around macroscopic yield strength (YS). **e-f** same as a-b for MgZn₂ grain boundary ‘cage’ precipitates. Notice the lesser magnitude of deviation in H6 as opposed to HIP. HIP is also much more abrupt, as opposed to H6’s gradual increase.

During loading, both the matrix and its precipitates deform. By simultaneously monitoring their respective XRD peak positions, the interplay between different phases can be mapped. Figure 32 presents the lattice strain deviation (defined as $\text{l.s.d.} = \epsilon_{\text{hkl}} - \frac{\sigma^{\text{applied}}}{E_{\text{hkl}}}$, [73]) along the loading direction for multiple families of reflections for the matrix, TiC, and the η precipitates in HIP (a, c, e) and H6 (b, d, f). Qualitatively, the two samples exhibit similar trends: both have positive matrix deviations before macroscopic yield, with $\{111\}$ having the highest magnitude, and both show a ‘hump’ behavior that occurs slightly after YS. The hump is caused by the deviation of lattice strain towards negative values, as a result of plastic relaxation. Concurrently, the precipitate peaks have strong positive deviations that increase sharply as the matrix reflections begin their downturn. A key difference between HIP and H6 is the rate at which this phenomenon takes place; in HIP the change is abrupt, whereas it is more gradual and less pronounced in H6.

The behavior is seen in both TiC and η ; however, the latter shows a much clearer trend for two reasons: i) TiC is much stiffer (~ 450 GPa) than η (~ 80 -100 GPa), making its deviation much harder to track, and ii) TiC has a volume fraction ($\sim 1\%$) that is about an order of magnitude smaller than η ($\sim 10\%$), thus reducing the XRD signal and worsening the quality of the peak fits. As shown in Figure 24, however, TiC and η mostly segregate at GBs’, thus their spatial distribution is taken to be indicative of the same load partitioning behavior.

Given the comparable grain distributions, TiC and η volume fractions, and their spatial arrangement along GBs across the two samples, the measured discrepancy in the magnitude of η lattice deviation in Figure 32 indicates intragranular mechanisms that are not resolved in SXRD. TEM-based analyses are used to investigate these features in the next section.

4.4.5 Deformed microstructure

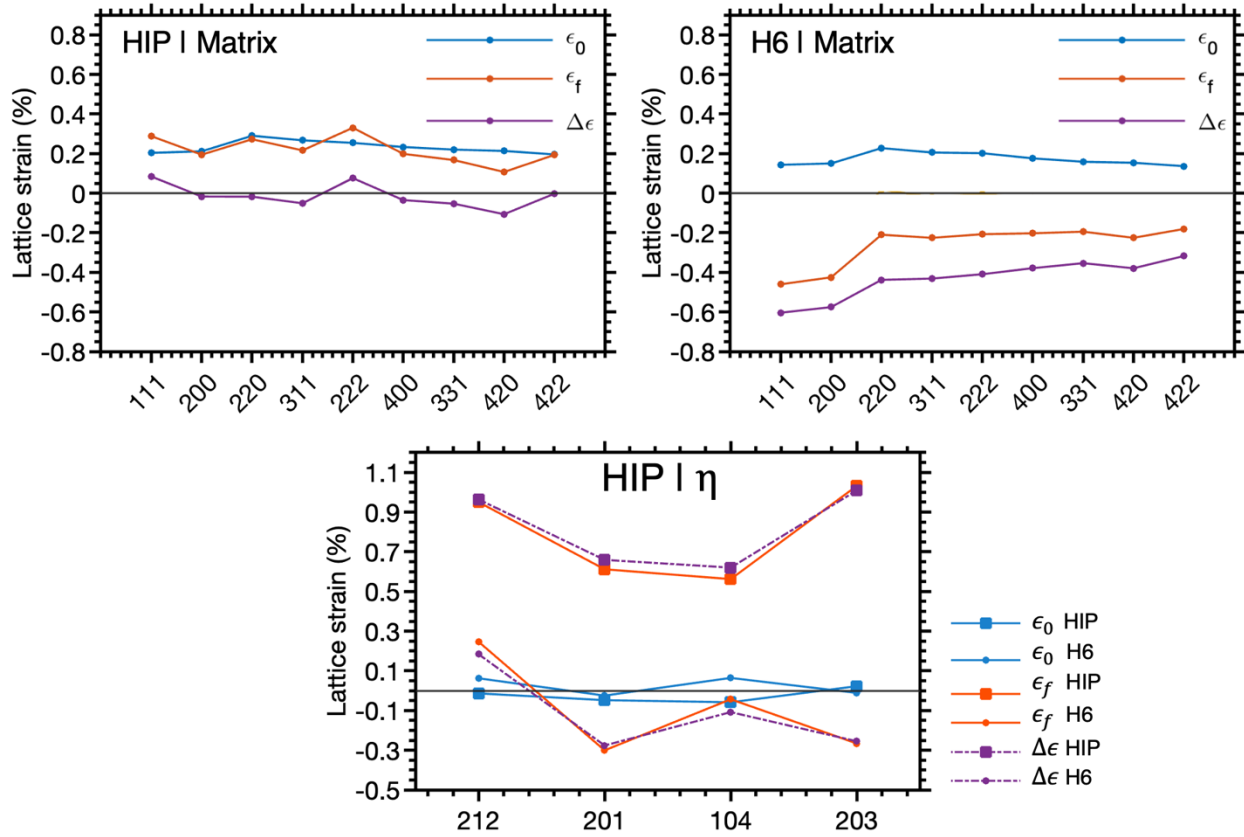


Figure 33 | Comparison of retained lattice strain post-fracture. a-b Initial strain (blue), post-fracture strain (red), and their difference (purple) for HIP and H6. HIP does not generate any left-over strain in the matrix after fracture, whereas H6 shows large compressive values. **c** MgZn_2 cage structure precipitates. The trend reverses relative to **a-b**, with HIP cage structure carrying a higher (positive) strain, whereas H6 hovers around zero.

Figure 33 reports the initial (blue) and post-fracture (red) values of lattice strain for all reflections ($\{111\}$ to $\{422\}$) for the matrix and η precipitates in HIP and H6. The initial values are almost identical in the two samples, both positive, at about 0.2% for most reflections. Since the reference lattice constant used for strain calculations was obtained via the Nelson-Riley extrapolation--which effectively erases small hkl dependent strain deviations--the absolute values

should not be used to draw significant conclusions. Instead, relative values provide a more reliable comparison.

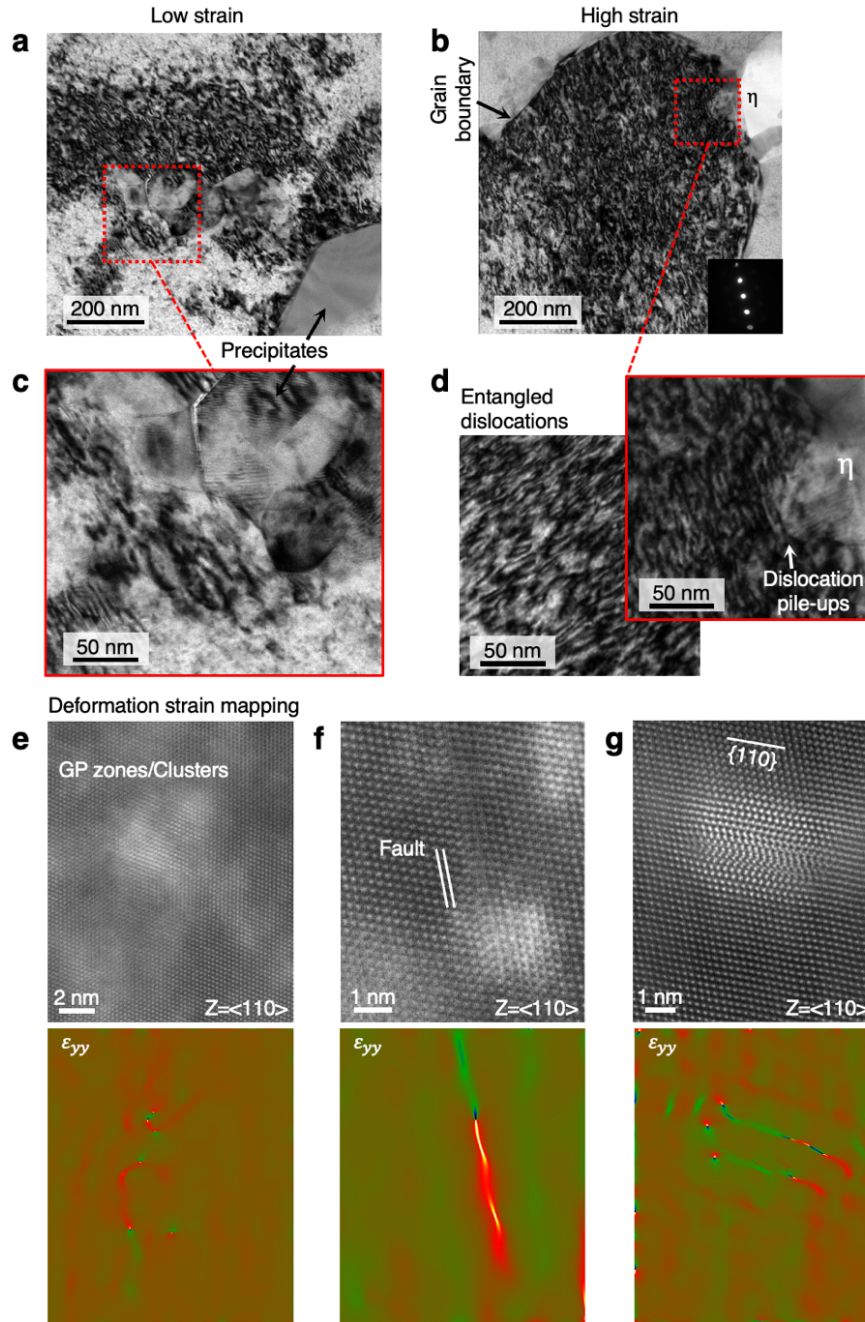


Figure 34 | Post-mortem transmission electron microscopy (TEM) deformation microstructure of H6 sample. a-c Dark field transmission electron microscopy (DF-TEM) images showing dislocations inside grains impinging on grain boundary (GB) cage precipitates. Further away from the fracture surface. **b-d** equivalent to **a-c** but closer to fracture surface, denser dislocation networks are observed, with entanglements and pileups forming within grains, at GBs and their precipitates. **e-g** High resolution (HR)

TEM and respective strain mapping showing three defects found in H6 postmortem, dislocations are seen inside and around GP zones/solute-rich regions **e**, faulting is observed between GP zone and the matrix **f**, and shearing/twinning inside a η' is revealed **g**.

The deformation induced strain differences are highlighted by the purple curves. HIP does not appear to retain any strain in its matrix reflections (aside from a small positive value for the 111 and 222 reflections). In contrast, H6 develops large internal compressive strains after fracture. The bottom subfigure displays an opposite trend for the large η precipitates, exhibiting large positive strains in HIP, as opposed to much smaller values in H6 (on average much closer to zero). These complementary trends show clear differences in the way stresses are redistributed during deformation in the heat-treated samples.

TEM analysis of the deformed microstructure for H6 is shown in Figure 34. Two regions on the fractured dogbone specimen were examined: one closer to the fracture surface ('High strain') and one farther from it ('Low strain'). The low strain sample shows a dense network of dislocations formed within the grains, often impinging on larger GB precipitates. In the high strain region, a similar behavior is observed, with more pronounced dislocation networks that often form pileups and elongated dislocation segments, both consistent with higher plastic strain.

Additional deformation signatures are found in H6. Three examples are presented in Figure 34c, alongside their respective strain mapping: (i) Dislocations are observed both inside and around GP zones/solute clusters; (ii) faulting is occasionally observed, spanning between the matrix and solute rich clusters; (iii) local distortions and faulting inside the age hardened η' phases, showcasing the plastic activity and contribution of these nanoscale precipitates to the system.

In contrast, TEM of the HIP sample revealed few deformation features. Dislocation accumulation was observed, similar to H6, however, no faults or slip traces inside or surrounding nanoscale precipitates or solute rich regions were observed.

4.5 Discussion

The three processing states analyzed in this chapter showcase a designed evolution of a TiC-inoculated AM 7xxx alloy with a highly non-equilibrium microstructure, to a hierarchically strengthened and mechanically optimized condition following heat treatments. Because grain sizes and TiC content are near identical in the three conditions, differences in deformation behavior are shown to arise from the presence of nanoscale solute-rich clusters, as well as age hardened precipitates and GB decoration. We connect the microstructural changes to the respective mechanical responses, and leverage in-situ SXR data to gain insight into the mechanisms responsible for the exceptionally high SUTS and significant ductility in the H6 condition.

4.5.1 *Effect of TiC on printability and microstructure*

TiC nanoparticle inoculation is central to both the printability and the microstructure of this alloy. Acting as heterogeneous nucleation sites, TiC suppresses dendritic growth during L-PBF in favor of a fine, equiaxed, nearly random grain structure, with mean grain sizes in the 1.6–1.9 μm range (Figure 23a–c). The fact that these grain sizes remain almost unchanged after HIP at 470 °C ($\sim 0.81 T_m$) and subsequent T6 aging (120 °C, 16 hrs) indicates that TiC pins GBs effectively and strongly suppress grain growth [20,41,46,47]. GB strengthening, then, can be considered stable across heat treatments.

The AP microstructure is a result of the extremely fast solidification, high solute content, and thermal cycling typical of L-PBF 7xxx alloys. SEM/EDS and TEM (Figures 23d and 24a, c) show extensive solute segregation along GBs and within grain interiors, with a dense network of coarse intergranular particles and chemically enriched regions, mainly segregated along GBs. XRD reveals their chemistry to contain MgZn_2 (η), AlCu_2Mg , and TiC in AP. At the same time, the rapid solidification and thermal history generate the highest initial dislocation density across conditions, as captured by the modified Williamson-Hall (m-WH) analysis, contributing to the alloy's strength.

High magnification TEM shows GP-zone-like clusters distributed within grains; in regions with very high local solute (e.g. GBs), thermal cycling during printing effectively acts as a low-temperature aging treatment. As a result, small η' precipitates appear near GBs in AP. However, these η' -like features are localized near GBs, and far less dense than in H6. Their incremental strengthening effect is therefore present, but likely minor, compared to the coarse GB network and cluster/GP strengthening.

Furthermore, AP's microstructure is highly constrained. The continuous GB precipitate/solute network, AlCu_2Mg , high initial dislocation density, and substantial GP/cluster population all contribute to its high YS, but at the cost of ductility. Uniform elongation is limited to $\sim 4\%$, consistent with stress localization at GB clusters, and residual porosity/stresses. In this state, the SS strengthening approximation listed in Table 6 is particularly uncertain: the SS term is computed assuming a uniform solute distribution in the matrix, but AP clearly violates this assumption, with much of the Mg, Zn, and Cu tied up in along GBs. As a result, the nominal ~ 97 MPa SS contribution is to be considered as a generous upper bound in AP.

4.5.2 Heat treated microstructures

The HIP process allows the alloy to retain its grain distribution, while thoroughly dispersing GB solutes to grain interiors. By exposing the alloy to 470 °C and 200 MPa, a significant fraction of the segregated GB solute is redistributed. Further, the process may alleviate internal residual stresses and minimizes porosity, thus enhancing ductility. As shown by EBSD maps, the grain growth is suppressed due to the TiC pinned boundaries; moreover, XRD now only show peaks for MgZn₂ and TiC, with AlCu₂Mg peaks essentially disappearing (Figure 23e, g). The dissolved GB solutes are driven back into the matrix, where they can form additional GP zones/clusters upon cooling.

While all three conditions contain nanoscale GP zones/solute-rich clusters, HIP likely carries a higher density relative to AP because more solute is dispersed into the microstructure during the treatment, and slightly higher compared to H6 due to some of the clusters being converted into η' during T6 aging.

The T6 treatment then adds a new level of hierarchy on top of the HIP microstructure. Solutionizing and aging (T6) transform the redistributed solute-rich clusters and GP zones into a dense population of nanoscale precipitates within grain interiors—the transition is partially shown in Figure 25d. The measured average “nanoscale precipitate” radius (~2.0 nm) and volume fraction (~1.25%) in H6 refer to all nanoscale precipitates/solute clusters visible in STEM—a mixture of GP zones, intermediate structures, and η' —rather than η' alone. FFT indexing and Zn/Mg maps (Figures 25–26) show the coexistence of GP1, GP2, transition structures, and η' , with η' appearing in Zn-rich regions and GP-like features persisting elsewhere [26]. Thus, HIP and AP already

contain a subset of these nanoscale precipitates/clusters; H6 simply pushes more of them along the GP to η' pathway, optimizing strength.

Along grain boundaries and triple points, HIP and H6 are remarkably similar. In both conditions, MgZn_2 appears as large precipitates at triple points and as smaller particles decorating GBs. In three dimensions, this can be visualized as an open ‘cage’ or ‘fishnet’ structure surrounding grains. This cage is fundamentally different from the AP state, where GBs are nearly completely encapsulated by a continuous precipitate/solute network. The XRD spectra for HIP and H6 overlap closely (Figure 23g), confirming that their GB MgZn_2 volume fraction and crystallographic signatures are very similar. T6 does not significantly “sharpen” or change the bulk amount of GB MgZn_2 ; rather, it mainly alters the intragranular nanoscale population by converting some clusters into η' .

Table 6 | Strengthening contribution to each material’s yield strength.

	AP	HIP	HIP+T6
	Strengthening ($\Delta\sigma$, MPa)		
σ_0	40	40	40
Grain Boundary	89	87	95
Solid Solution	<<97	<97	<97
Dislocation	86	60	68
Precipitation (Orowan)	-	-	388
Predicted yield (MPa)	312	284	688
Measured yield (MPa)	523	515	674
Difference (MPa)	211	231	14

From the standpoint of the strengthening model, the SS term is better justified in HIP and H6 than in AP. In HIP, solute is more uniformly distributed in the matrix after dissolution of GB films, so treating the measured composition as an upper-bound SS contribution is reasonable. In H6, some solute is sequestered into η/η' and GP zones, so the same SS term again represents an upper bound; the true SS strengthening is somewhat lower, but the missing contribution reappears in the explicit precipitation term computed from the measured r and f . Overall, the SS approximation is worst in AP, more realistic in HIP, and upper-bound but internally compensated in H6. Nonetheless, the respective contributions are not the dominant mechanisms and are likely within a few tens of MPa's of each other, rendering their direct comparison reasonable.

4.5.3 Strengthening effects of heat treatments

The strengthening analysis in Section 4.3.3 allows a quantitative comparison between predicted and measured yields and highlights how much strengthening is already present in HIP before η' is introduced.

Table 6 summarizes the initial strengthening contributions to YS for the three samples. AP and HIP show summed values of 312 MPa and 284 MPa, where the effect of potential precipitation strengthening is excluded. These values are considered as the precipitate-free baseline. The 'difference' row computes the remaining strengthening needed to match the experimentally measured YS's. The small discrepancy between HIP and AP likely arises from the overestimation of SS in AP, and the presence of some η' precipitation in AP. Additionally, the closed cage structure in AP likely hinders dislocation motion more effectively, increasing YS at the cost of ductility. In HIP the strength difference must be generated partly by the denser nanoscale solute-rich clusters (also present in AP and H6), coupled with the more open-cage structure that decorates

boundaries and triple points. The open cage geometry allows for simultaneous strengthening and work-hardening, thus retaining similar YS values and optimizing uniform elongation, both of which are observed in the mechanical properties.

In H6 the precipitate-free baseline (300 MPa) is similar to that of AP and HIP. The precipitation term computed via Orowan looping for the measured nanoscale population (which includes all nanoscale clusters and precipitates, not just η' , is calculated to be about 388 MPa, yielding a total predicted yield of ~688 MPa, in good agreement with the measured value of ~674 MPa.

However, a crucial point is that the 388 MPa Orowan value should be interpreted as the total effective precipitation strengthening in H6 relative to a hypothetical precipitate-free matrix, not as the incremental strengthening over HIP. The measured yield difference between HIP and H6 is only ~160 MPa (674–515 MPa), not 388 MPa. This implies that roughly ~229 MPa of the precipitation strengthening captured by the Orowan model is already present in HIP, via the GB η cage and the GP-like/cluster network, leaving only the remaining ~160 MPa as a direct result of the age-hardening process. The difference is in good agreement with the tabulated values.

This interpretation is consistent with three main observations:

1. HIP and H6 share nearly identical GB η morphologies and volume fractions. The “cage” effect of GB η large particles at triple points and smaller ones along GBs is present in both and should therefore contribute similarly to both HIP and H6 strengthening.
2. HIP contains a dense network of non- η' precipitates—also present in AP and H6, to a lesser extent. The fact that HIP does not show strong residual intragranular deformation

signatures (Section 4.3.4.3) suggests that these non- η' nanoscale obstacles are not the dominant source of additional strengthening beyond the GB cage in HIP.

3. H6 is the only condition that clearly adds a dense intragranular η' population and shows direct nanoscale precipitate deformation post-mortem. The ~ 160 MPa difference between HIP and H6 is therefore reasonably attributed to the incremental effect of η' and the way it redistributes load and plasticity, on top of a GB-cage-dominated strengthening framework common to both.

In other words, the Orowan term (388 MPa) in H6 is overestimating the strength contribution from the mechanism despite the close agreement with observed YS values. This is because a significant portion of its non- η' nanoscale precipitates (included in Orowan calculations), are shown to not –independently-- strengthen the material significantly (as evidence from HIP TEM). However, once coupled with η' precipitates, they take on additional load, relaxing the load carrying need from the cage effect at GBs. Lattice strain deviation confirms this shift on load-partitioning away from GBs, and in favor of grain interiors (TEM).

The mechanistic sequence inferred from SXRD and TEM is summarized in Figure 35.

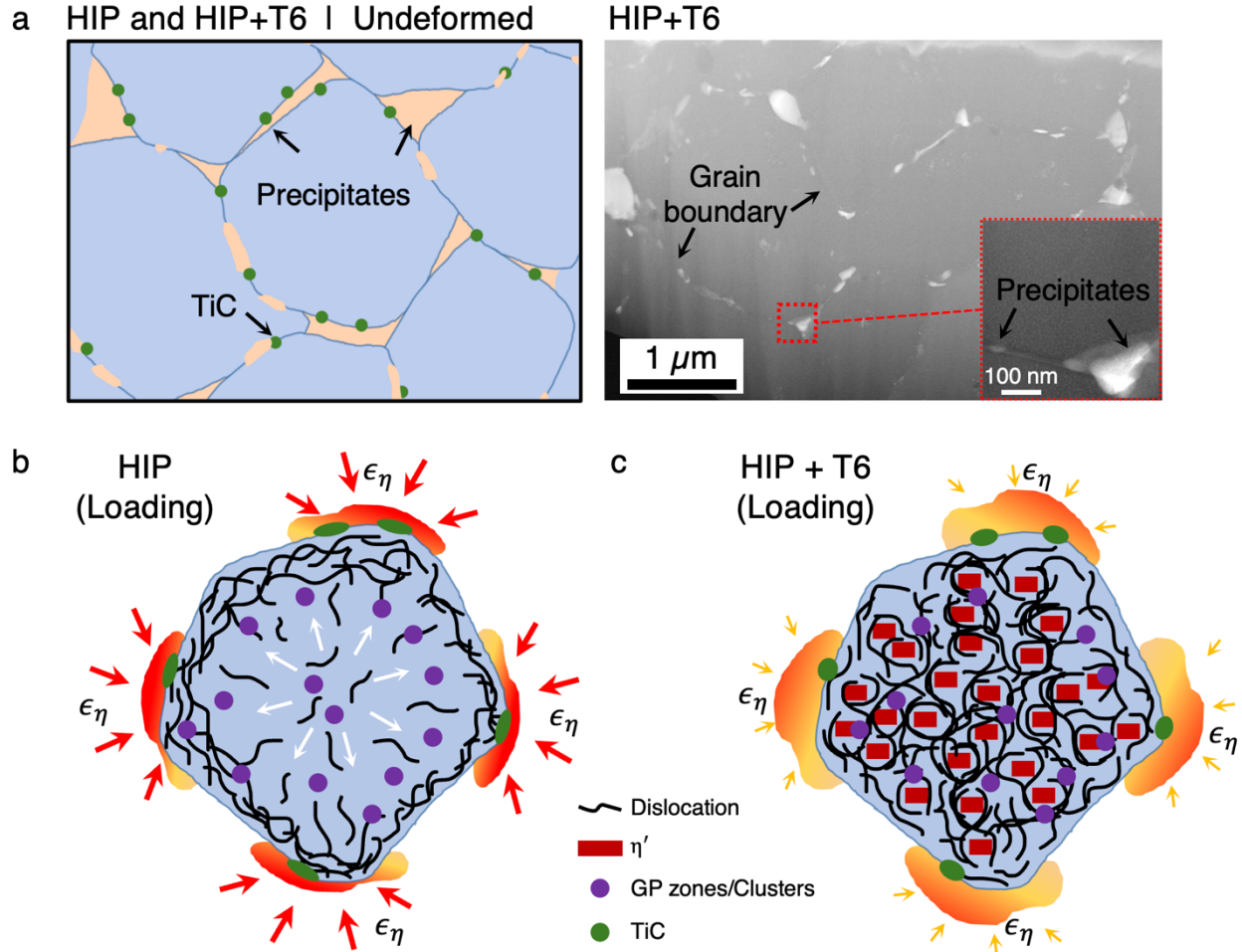


Figure 35 | Schematic of open cage structure deformation. **a** Schematic and respective transmission electron microscopy (TEM) image showing a representative grain structure of the HIP and H6 samples. Grains are surrounded by an ‘open cage’ η grain boundary (GB) structure **b**. Deformation in HIP showing dislocations generate inside grains multiplying and quickly migrating, and impinging on, the GB cage structure, shedding large amounts of the stress onto it. **c**. Same as **b** but following a peak-age T6 treatment. A dense network of age-hardened precipitates hinders dislocation motion, strengthening the material further, while repartitioning load away from the GB cage.

Figure 35a juxtaposes a schematic of the heat-treated microstructure with a representative TEM image from H6. At this scale, the arrangement and size of the larger GB η precipitates and TiC particles are essentially the same in HIP and H6, so only the H6 condition is shown

schematically. Both states share a TiC-pinned, fine grain structure surrounded by an “open cage” of η along boundaries and at triple junctions.

Figures 35b and 35c illustrate the different ways in which HIP and H6 accommodate load. In HIP (Figure 35b), dislocations nucleate and glide relatively freely within grain interiors, interacting primarily with GP zones/clusters but not with a dense intragranular η' network. As strain increases, dislocations pile up at the GB cage, and load is abruptly transferred to the grain-boundary precipitates, which carry most of the deformation. This is consistent with the large η lattice-strain deviations that ensue right after YS, as well as the residual tensile strains in HIP η , but not present in the HIP matrix. In H6 (Figure 35c), a dense population of intragranular η' precipitates (schematically enlarged for clarity) and solute clusters partition the load more uniformly inside grain interiors. Dislocations are repeatedly pinned and redirected inside grains, so that plasticity is shared between the matrix, GB η and nanoscale η' /clusters. This picture matches the gradual η lattice-strain evolution in H6, the retained compressive residual strains in the matrix post-fracture, and the nanoscale precipitate deformation features seen in TEM.

4.5.4 Dislocation evolution

The dislocation evolution measured by in-situ SXR (Figures 30, 31) provides an independent probe of how these microstructures carry load.

In AP, dislocation density increases monotonically with stress, with a modest increase near YS, but no apparent post-yield plateau. This is consistent with a microstructure where dislocation motion is strongly constrained by continuous GB networks and inhomogeneous solute distributions: dislocations multiply and pile up, but there is no refined intragranular precipitate

hierarchy to help redistribute load. Combined with residual porosity and GB films, this leads to high YS but poor ductility. AP's initial highest dislocation density contributes to the effect.

HIP's behavior is more complex from the early stages of deformation. In the macroscopic elastic regime, the dislocation density shows a slight negative trend, suggesting partial annihilation or rearrangement of residual defects introduced during heat treatment. Given that HIP is performed at a temperature and pressure high enough to plastically deform the alloy, dislocations can be locked in non-equilibrium configurations; upon re-loading in tension, some of these configurations relax, potentially reducing defect density and their net broadening effect measured under SXRD. Past this initial stage, dislocation density in HIP increases sharply near YS. The much lower initial dislocation density, coupled with the less restrictive boundary precipitate arrangement and lack of any η' precipitation, allows dislocations to form and migrate almost unhindered. Dislocations multiply quickly and pile up at boundaries, abruptly shedding load from grain interiors to the larger GB precipitates [97,106,111,113,114]. This step is corroborated by the sudden positive deviation in η precipitates and simultaneous downturn of matrix planes deviation. After the plateau load distribution equilibrates, grain interiors begin deforming again (large work hardening), as the elastic strain of the η precipitates saturates and slows. This concept is further explored in the next section.

H6 exhibits the same qualitative trends—pre-yield increase, post-YS plateau, and subsequent linear rise—but with larger absolute densities and higher accumulation rates post-yield. The existence of a plateau just after YS in both HIP and H6 is informative: during this interval, the materials continue to strengthen and elongate macroscopically, even as matrix dislocation density temporarily stagnate. This behavior requires an alternative sink for load and plastic

deformation—an inference that is directly supported by the lattice strain and residual strain analyses.

4.5.5 Lattice strain, load partitioning, and residual stress states

Lattice-strain deviation and residual strain measurements (Figures 32–33) clarify how load is partitioned between matrix and precipitates in HIP and H6. Before macroscopic yielding, both samples display positive lattice-strain deviations in matrix reflections, especially $\{111\}$, as grains favorably oriented relative to the loading direction carry higher elastic loads. This is consistent with the pre-yield rise in dislocation density and the $\{111\}$ intensity changes seen in Figure 30.

As stress exceeds YS, the matrix lattice-strain deviations exhibit a hump: they increase slightly beyond the elastic expectation, then decrease even as the applied stress continues rising. At the same time, η reflections develop strong positive deviations, indicating that GB MgZn_2 is taking on increasing fractions of the applied load. This is true for both HIP and H6, confirming that in both conditions the GB η “cage” acts as a major load-bearing mechanism.

HIP and H6 differ mainly in the rate and distribution of this load transfer. In HIP, the matrix deviation drops and η deviation rises abruptly, implying a sudden partitioning of load from the matrix to the GB cage. In H6, the transition is more gradual and the η deviations are systematically smaller. Given that GB η volume fraction and connectivity are similar in HIP and H6, this reduced η load in H6 can only be explained if a significant portion of the load is being absorbed by intragranular obstacles—namely η' and the remaining nanoscale clusters/GP zones.

Residual lattice-strain data at fracture (Figure 33) reinforce this picture. In HIP, the matrix reflections show almost no net residual strain, whereas η exhibits large positive residual strains,

indicating that upon unloading the matrix relaxes while GB η remains deformed and stores most of the internal stress. This will be validated by TEM and presented in 4.4.6. In H6, the matrix reflections show significant compressive residual strains, while η residual strains are much smaller and closer to zero. This trend inversion means that, in H6, plastic strain and internal stress are more broadly distributed within grain interiors and near nanoscale obstacles, rather than being concentrated only at GB η .

Taken together, these results suggest that HIP and H6 share the same GB cage effect, but H6 partially relieves that cage by enabling η' and clusters inside grains to participate in load sharing. The ~ 160 MPa incremental YS and the different residual strain states thus arise from how much of the total precipitation strengthening is carried by the GB cage alone (HIP) versus being shared with a finely distributed intragranular η' /cluster network (H6).

4.5.6 TEM signatures of intragranular deformation in H6

Post-mortem TEM of H6 directly confirms that intragranular features carry a substantial portion of the plastic deformation. In both low-strain and high-strain regions, dislocation networks are observed within grains and impinging on GBs and GB η precipitates, as expected for a GB-strengthened alloy. In high-strain regions, pileups and elongated dislocations are more pronounced, reflecting the higher local plastic strains reached before fracture.

Beyond this, H6 shows deformation features that are essentially absent or much weaker in HIP. Strain mapping and high-resolution images reveal a combination of:

1. Dislocation traces nearby and/or inside GP zones/solute clusters;
2. Faults that span from the matrix into solute-rich clusters;

3. Local distortions and faulting within η' precipitates.

These observations show that clusters and η' are not passive obstacles in H6, but actively store plastic strain—this confirms the compressive residual strains in the matrix and the more modest/almost absent relative to HIP, residual strains in η .

In HIP, TEM reveals dislocation accumulation and pileups at GB η like those in H6, but no clear evidence of faults or slip traces within nanoscale precipitates or clusters. This suggests that while non- η' nanoscale features exist and contribute to strengthening, they do not act as major intragranular plasticity carriers, abruptly shifting the load to the GB cage, which carries a significant amount of the precipitation-related load. This is consistent with the idea that the ~230 MPa of precipitation strengthening already present in HIP comes primarily from the GB η cage and cluster network, while the additional ~160 MPa increment in H6 is tied to η' -enabled intragranular accommodation.

4.5.7 *Strength–ductility synergy in H6: mechanisms*

The combined microstructural, SXRD, and TEM results can be summarized by the following key take-aways:

- AP: TiC inoculation delivers a fine equiaxed grain structure but, most strengthening arises from a continuous, highly heterogeneous GB precipitate/solute network, eutectic AlCu₂Mg, high initial dislocation density, and a non-uniform GP/cluster population. SS strengthening is overestimated by the simple composition-based model because solute is not uniformly dispersed. The microstructure is strong but much more brittle: plasticity is restricted by the continuous cage, still contributing to YS, but severely limiting ductility

and work hardening. Porosity and residual stresses are likely to play a significant role in reducing the ductility of this material.

- HIP: The high temperature and pressure treatment removes porosity, reduces residual stresses, dissolves GB (eliminating AlCu₂Mg completely) into the matrix, and develops a GB η "open cage" structure, alongside a richer intragranular GP-like/cluster population, all while TiC prevents grain growth and therefore retains the broader grain distribution. Precipitation strengthening of ~230 MPa is already present, largely from the GB cage and cluster network. Under load, deformation transitions from matrix slip to a regime dominated by abrupt load transfer to the GB η cage, as seen in the sudden η lattice-strain increase and the large positive residual η strains. The result is a significant improvement in ductility relative to AP, with yield strength comparable to AP but much higher uniform elongation and work hardening capacity.
- H6: Peak aging achieves a dense intragranular η' population on the HIP microstructure, partially transforming cluster aggregates while leaving the GB cage essentially unchanged. The total precipitation strengthening in H6 is ~388 MPa, but only ~160 MPa of this is incremental over HIP—the remaining ~230 MPa is shared with the GB cage framework already present in HIP. What changes is not only the magnitude of strengthening, but the way plasticity is accommodated: load transfer from matrix to precipitates occurs more gradually, GB η carries less of the final load, and intragranular η' and clusters store much of the residual strain (generating post-fracture compressive strains). This redistribution is directly reflected in the lattice-strain evolutions, residual strain inversions, and matrix nanoscale deformation signatures in TEM. H6 therefore achieves a rare combination of very high yield strength, the highest reported specific tensile ultimate strength, and large

uniform elongation, by combining a TiC-stabilized ultrafine grain structure, an open GB cage structure also seen in HIP, and a finely tuned η' /cluster network that enables intragranular plastic accommodation instead of merely intensifying GB stress.

In this framework, the strength–ductility synergy in H6 is not simply due to the textbook precipitation strengthened mechanisms. Rather, it emerges from how η' is added to an already cage-strengthened HIP microstructure: η' provides the extra ~ 160 MPa of yield strength while simultaneously shifting part of the plasticity burden from GB η to the grain interior, delaying localization and enabling extensive work hardening.

4.6 Summary

This chapter demonstrates that combining nanoparticle-assisted solidification with sequential HIP and T6 heat treatments enables a new class of ultra-high-strength additively manufactured 7xxx alloys. The AP condition shows that rapid solidification supported by TiC inoculants produces a refined, equiaxed, crack-free microstructure with ultrafine grains. However, high residual stresses, solute segregation, and heterogeneous eutectic remnants limit ductility and lead to premature strain localization and failure. HIP homogenizes the matrix chemistry, removes porosity, and releases residual stress while retaining the ultrafine grain structure pinned by TiC. This treatment enables the impressive strength–ductility balance observed in HIP, despite the absence of nanoscale age-hardening phases.

The T6 condition (H6) builds upon this foundation and achieves a simultaneous gain in specific ultimate tensile strength that surpasses conventional and AM Al-Zn-Mg-Cu alloys and even conventional Ti-6Al-4V. The dominant strengthening mechanism arises from a nanoscale network of η' precipitates and solute-rich clusters with Orowan looping identified as the active

bypass mechanism. Importantly, this nanoscale contribution does not replace the boundary-controlled “cage strengthening” already active in HIP; rather, it complements it by distributing stress and plasticity among matrix, grain-boundary η , and intragranular η' . This load sharing was revealed through in-situ SXR by the post-yield partitioning of lattice strain between matrix and GB precipitates, as well as large compressive residual strains in the H6 matrix after failure. TEM confirms that only the aged microstructure retains pervasive nanoscale intragranular deformation signatures — including dislocation pinning by η' , sporadic stacking faults between matrix and nanoscale solute-rich clusters, and η' faulting.

Altogether, the results provide a unified mechanistic framework: TiC nanoparticles refine grains and suppress hot tearing and grain growth, enabling printing of an otherwise ‘unprintable,’ high performance alloy; the GB open cage structure formed in HIP stabilizes grains, mediates load transfer, and contributes substantially to yield strength and work hardening ability; η' peak aged precipitates in H6 activate intragranular nanoscale deformation storage and smooth the transition from elasticity to plasticity, enabling high work-hardening and delayed localization.

The synergy of all these mechanisms is responsible for the exceptional performance of the aged AM alloy.

4.7 Future Work

A more detailed understanding of these alloy’s deformation mechanisms can be gained by addressing the following points:

- i. High temperature testing can reveal the thermal stability of the system due to the cage structure (already shown to withstand temperatures up to 120°C for 16 hours)

and the presence of TiC nanoparticles. This can be achieved either by regular mechanical testing, or a combination of in-situ SXRD mechanical testing at elevated temperatures;

- ii. Creep and fatigue testing can reveal the mechanics of deformation. Small grain sizes tend to have detrimental effects due to the higher chance of GB slip; however, the pinning role of TiC may affect these behaviors substantially, opening possibilities for ultra-high specific ultimate strength alloys in harsher environments;
- iii. Plasticity model incorporating the dynamics of the GB cage effect, in combination with SXRD results, can further shed light on the unfolding mechanisms and load partitioning behavior of the systems at different treatment conditions;
- iv. Optimization of TiC nanoparticles size, distribution, and quantity may further improve the already exceptional mechanical properties reported in this work.

Chapter 5. Synchrotron X-ray diffraction of other material systems

5.1 Introduction

In-situ synchrotron X-ray diffraction (SXRD) enables real-time tracking of lattice-scale deformation in metals, revealing how defect accumulation, lattice elasticity, and crystallographic reorientation evolve under load. For FCC alloys — particularly those produced by laser powder-bed-fusion (L-PBF) — these measurements provide critical insight into deformation paths that may differ from conventionally processed microstructures. However, correct interpretation of in-situ signals requires careful attention of the diffraction reflection-dependent behavior of metals and its connection to intrinsic material properties [97,98,108,160].

For instance, lattice strain evolution during plasticity can be influenced by elastic anisotropy and stacking-fault energy (SFE) of a material [125,161–163]. Materials with higher anisotropy factors tend to show larger lattice strain difference among reflections; grain families with lower directional stiffness tend to carry more load elastically and therefore deviate earlier or more strongly under tension. Lower SFE increases the tendency for partial dislocation activity and associated defects (e.g., stacking faults and twins), which is known to affect the relative behavior of pairs of parallel reflections (e.g. 111/222, 200/400). Thus, differences in SFE and anisotropy together shape the ordering and magnitude of the lattice-strain trends observed in SXRD (Table 8), [11,21,73,97,98].

The AM systems investigated in this work — pure Cu, CoCrNi, SS316L, and a nanoparticle-modified AA7075 alloy — span a wide range of SFE and elastic properties, providing a systematic comparison of SXRD interpretability. Copper, being a single-phase system, supports a reliable dislocation-based interpretation and enables validation of defect-density quantification

using a modified Williamson–Hall (m-WH) approach. CoCrNi and 316L introduce increasingly concentrated solid-solution strengthening, allowing us to examine how reduced SFE and increased cross-slip resistance alter lattice-strain divergence across reflections. Finally, AA7075 represents the most microstructurally complex case, where hierarchical solute clustering and precipitation (Chapter 4) showcase SXRD potential for monitoring phase-dependent load sharing. Moreover, we discuss the value of collecting SXRD data over a wider azimuthal range. Using AA7075 as a case study, 180° directional mapping of lattice deviation and intensity evolution illustrates how deformation varies as a function of spatial orientation. Proper quantification and interpretation of this data is highly relevant for micromechanical modeling applications and interpretation of near-isotropic plasticity.

This chapter highlights how intrinsic material properties dictate the way in-situ SXRD signals evolve, and how understanding these dependencies, and their detection limitations, can inform more advanced microstructural design. The comparisons presented here establish a well-rounded framework, providing insight into microscopic deformation behavior across AM FCC materials with vastly different SFE (Table 8), elastic properties, and microstructural complexity.

5.2 Experimental

Equiatomic CoCrNi medium-entropy alloy (MEA) samples were produced by laser powder-bed-fusion (L-PBF) using an AM 400 system (Renishaw plc, United Kingdom) equipped with a 400 W laser and a 70 μm focal beam diameter. Rectangular blocks (36 mm length $\times$ 20 mm width $\times$ 15 mm height) were fabricated on a steel build plate. The chamber atmosphere during printing was maintained under high-purity argon with oxygen levels below 0.1%.

The gas-atomized CoCrNi powder exhibited a particle size distribution of 15–53 μm , with an average size of $\sim 36 \mu\text{m}$. A meander scan strategy was used, rotating the scan vector by 67° after each layer. Processing conditions included a pulsed laser power of 200 W, exposure time of 80 μs , point distance of 60 μm , hatch spacing of 90 μm , and a layer thickness of 50 μm .

L-DED 316L stainless steel samples were produced using a LENS® 150 system (Optomec Inc., Albuquerque, NM). Rectangular deposits measuring 40 mm $\times$ 10 mm $\times$ 40 mm (length $\times$ width $\times$ height) were built on a 10 mm thick 316 stainless steel substrate under argon shielding at a flow rate of 20 L/min. The 316L powder feedstock followed a Gaussian particle size distribution between 45 and 106 μm , delivered at 2.4 g/min. Processing conditions consisted of a 300 W laser, a beam diameter under 1 mm, a scan speed of 8.4 mm/s, and a hatch spacing of 380 μm , using a meander raster pattern. The resulting layer height was 250 μm . All printing parameters are tabulated below.

L-PBF Cu was printed with the parameters specified in [164], and AA7075 parameters can be found in the experimental section of Chapter 4. All samples were then cut into dogbone geometry via electric charge discharging (EDM) to match the geometry required by the RAMS2 pin-held system at Cornell High Energy Synchrotron Source (CHESS, beamline ID3a). Samples were pulled at a constant strain rate of between $2\text{--}3.5 \times 10^{-5}$.

Table 7 | Printing parameters used in this chapter

	Machine	Laser size (μm)	Laser power (W)	Laser speed (mm/s)	Hatch spacing (μm)	Layer thickness (μm)	Exposure time (μs)	Point distance (μm)
AA7075 (Scan 1)	1	70	170	–	120	30	50	30
AA7075 (Scan 2)	1	70	300	–	110	–	25	30
CoCrNi	1	70	200	–	90	50	80	60
SS316L (L-DED)	2	<1000	300	8.4	380	250	–	–
Copper	3	60	200	500	30	20	–	–

1: Renishaw AM400; **2:** LENS[®] 150 system; **3:** BLT-S210

5.3 Results and discussion

5.3.1 Orientation dependence via SXRD

To build upon the in-situ interpretation established in Chapter 4, the HIP-treated AA7075 sample is used here to expand on SXR D capabilities. The system's fine, equiaxed grain distribution, negligible texture, and highly statistical sampling renders it well-suited for representative SXR D investigation.

Beyond the loading direction (LD) alone, orientation-dependent deformation trends using 180° azimuthal mapping of lattice strain deviation and normalized intensity are displayed in Figure 35. Even in a material that exhibits a statistically isotropic microstructure at the macroscopic scale, these maps reveal directional variations in elastic/plastic response and grain reorientation. Three families of reflections are presented to highlight the hkl-dependence of the alloy's response to

external tensile stresses. Notice, for instance, the simultaneous increase in relative intensity of 111 and 200. Intensity does not only change along LD, but increases are also noticed roughly 70° away from LD, in a symmetrical fashion. The relationships offer insight into the geometrical dependencies of grain reorientation relative to LD. Simultaneously, in the lattice strain deviation plots, a clear transition between positive and negative values is seen (contour lines in white, value of zero), delineating regions and strain levels where perfect elastic behavior is obtained. In general, there appear to be geometrical correlations between the two sets of maps; SXRD behavior must then be evaluated with attention to spatial orientation, as subtle differences in deformation pathways can be overlooked when relying solely on a single scattering direction (i.e. LD).

With AA7075-HIP showcasing the precision of the SXRD approach and the need to consider directional effects, the following sections examine how lattice strain trends evolve in other FCC systems with different intrinsic properties — including slip geometry, stacking-fault tendency, and defect landscapes — to evaluate how material-specific behavior influences the interpretation of SXRD data [94,96–98,101,102,105,107–109].

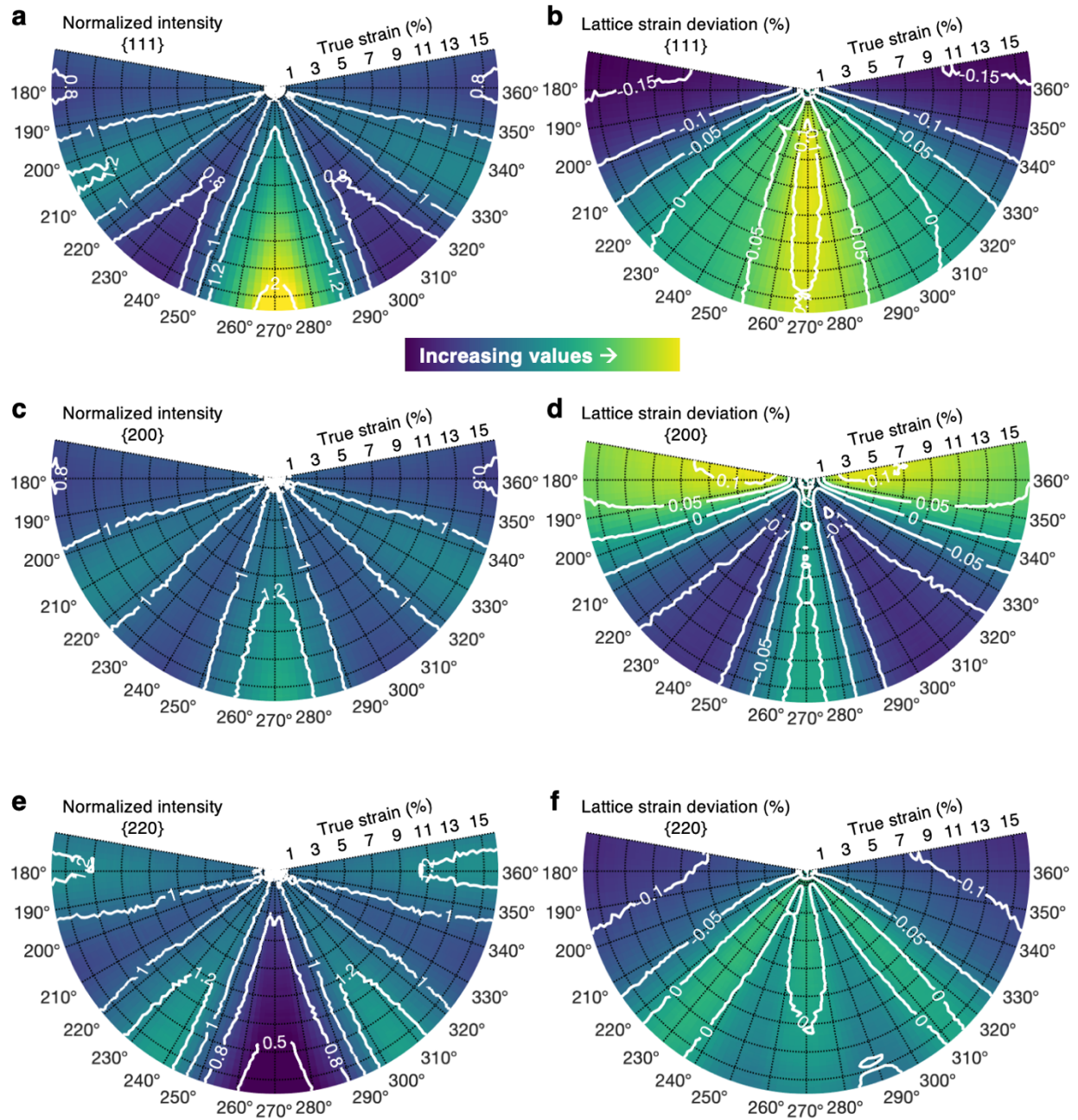


Figure 36 | Azimuthal mapping of texture and lattice strain evolution in AA7075-HIP. a, c, d Polar maps of normalized texture evolution for {111}, {200}, and {220} planes, respectively, as a function of applied true strain. The colormap is shown (blue to yellow) and increases on a linear scale. White contour lines delineate stated values. **b, d, f** Same type of plot, but for lattice strain deviation.

5.3.2 The effect of anisotropy

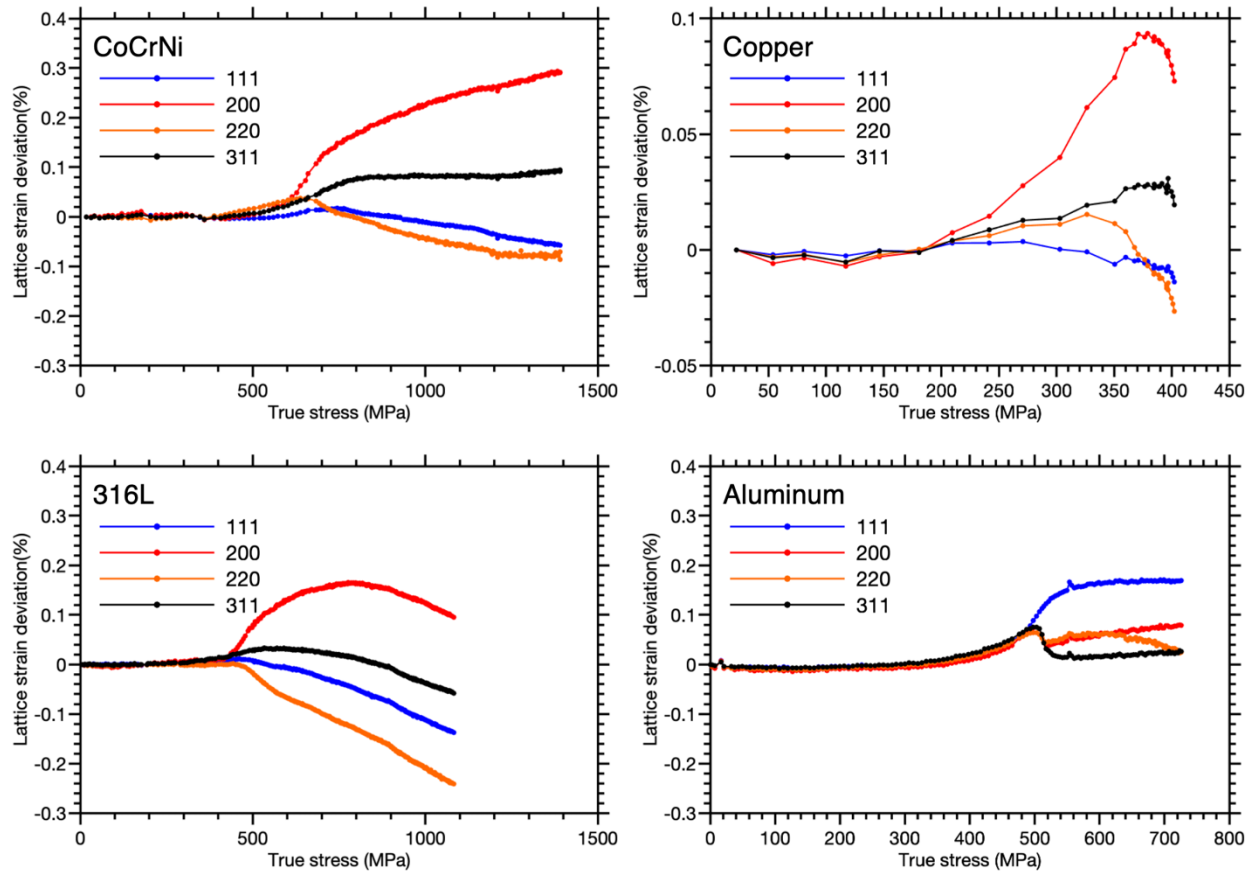


Figure 37 | Lattice strain deviation evolution for 4 FCC materials along loading direction (LD). Four diffraction reflections are plotted, as shown in the legend. A trend of smaller deviation as elastic anisotropy decreases is observed. Aluminum shows different behavior in the $\{111\}$ planes, which deviate the most, unlike other systems. Notice that Cu data has a different y-axis relative to other materials.

Lattice strain deviations along the LD provide a direct view into how load is partitioned among crystallographic directions across all stages of tensile loading. The degree of elastic anisotropy plays a dominant role in determining the hkl-dependent response of the system. In near isotropic systems (i.e. Aluminum, $A=1.22$, $C_{12}/C_{44}=1.045$) the lattice strain deviation curves tend

to track closely together [73,98,110]. As the anisotropy increases, specifically the C_{12}/C_{44} ratio, the relative lattice strains begin to diverge — signaling that, in general, more compliant orientations carry disproportionately larger elastic loads (Table 8 tabulates A, C_{12}/C_{44} , and SFE).

The AA7075-HIP sample, with elastic anisotropy very close to unity, shows the tightest clustering of deviation curves ($\{111\}$, $\{200\}$, $\{220\}$, and $\{311\}$), shown in Figure 36. This behavior matches expectations for aluminum’s intrinsically near-isotropic FCC stiffness (Table 1, 4). AM Cu and 316L exhibit a modestly greater spread in the strain deviations; $\{200\}$ carries more elastic load while $\{111\}$ remains closer to a purely elastic response. Importantly, this qualitative ordering matches the available literature for pure Cu and 316L, validating that the AM processing route does not necessarily erase the underlying crystallographic relationships during early deformation [97,98].

CoCrNi, which possesses the greatest C_{12}/C_{44} value among the systems considered, displays the largest separation in lattice strain deviation curves (Figure 36), with the $\{200\}$ family deviating substantially more than $\{111\}$ in magnitude (0.3% vs. <-0.06%, respectively.)

The progression of relative deviation separation observed experimentally (CoCrNi > 316L > Cu > AA7075) is consistent with the relative elastic properties extracted from the measured elastic constants reported in Table 1 and reproduced below.

Table 1 | Measured $\{hkl\}$ dependent Young's Moduli (GPa) for four 3D printed materials.

	$\{111\}$	$\{200\}$	$\{220\}$	$\{311\}$	$\{222\}$	$\{400\}$	$\{331\}$	$\{420\}$	$\{422\}$
Al (H6)	73.85	68.05	72.37	70.3	75.6	71.6	73.3	72.9	75.1
Al (HIP)	79.3	75.7	80.3	78.2	83.2	76.3	82	80.1	82.5
Al (AP)	79.5	76.2	78.9	78.6	82.1	77.6	79.67	78.7	80.4
Cu	156.4	109.3	145.8	129.5	163.8	109.3	151.7	133.9	151.6
316L	245.6	149.9	209.3	187.5	247.6	149.2	238.6	200.2	236.9
CoCrNi	282.5	157.9	253	202.1	279.7	150.4	284.6	219.2	244.8

The HIP AA7075 data shown share comparable trends to the literature, where notably, the $\{111\}$ reflection along LD deviates the most—in contrast with Cu and 316L. However, the system in this work shows deviations across all families increasing positively before YS. This discrepancy with the literature likely reflects AM-specific microstructural features. Specifically, the complex microstructural landscape created by TiC-stabilized grain refinement, as well as the well-dispersed network of nanoscale solute-rich clusters. Coupled with strong load partitioning (Chapter 4) the microstructure seems to promote nearly simultaneous activation of load shedding across all reflections. Nevertheless, the reduced family-to-family separation is what is expected for a highly isotropic FCC metal, confirming that the HIP state acts as an excellent benchmark for interpreting SXRD lattice strain behavior.

Table 8 | Anisotropy factors from elastic properties for four FCC systems

	Al	Cu	316L	CoCrNi
A	1.22	3.21	3.77	3.05
C_{12}/C_{44}	1.045	1.43	1.64	1.79
SFE	124 mJ/m ² [165]	58 mJ/m ² [163]	32.8 mJ/m ² [162]	15.1 mJ/m ² [162]

5.3.3 *The effect of stacking fault energy*

In FCC systems, dissociation of perfect dislocations into Shockley partials introduces local disruptions in the close-packed $\{111\}$ planes. These stacking faults alter the elastic response recorded by SXRD peak positions. As plastic deformation progresses, the lattice-strain evolution reflections that share the same crystallographic direction — such as $\{111\}$ and $\{222\}$ — begin to diverge once faulting becomes active. The difference in their strain evolution therefore provides a practical signature of stacking-fault probability (SFP) during in-situ loading [125,130,162,166–170].

Across the four FCC metals investigated here, the magnitude of 111/222 strain divergence shows a clear progression that mirrors their known SFE values. CoCrNi, with the lowest SFE of the group, develops the widest separation between the two reflections (Figure 36). 316L follows with a smaller but still distinct divergence, consistent with partial formation contributing to planar deformation. Cu shows only a modest separation, in line with medium SFE and a deformation mode dominated by full dislocation glide. Finally, AA7075-HIP, which exhibits the highest SFE among all systems studied, shows essentially no measurable difference between the two families' lattice-strain trajectories.

This CoCrNi > 316 > Cu > Al ordering reinforces that lattice strain divergence between $\{111\}$ and $\{222\}$ is a useful in-situ marker for the extent to which stacking-fault-mediated plasticity contributes to work hardening. The AM Cu response is particularly informative in this context: its relatively small SFP separation confirms that most broadening can be interpreted as arising from strain-related dislocations rather than planar faults, providing confidence that the m-

WH analysis yields physically meaningful trends in a system where the strengthening mechanism is well understood and largely governed by dislocation storage.

Taken together, these SXRD observations show that interpreting lattice-strain evolution in different FCC alloys requires close consideration of intrinsic material properties — particularly SFE and elastic constants— to avoid misattributing defect signatures that originate from fundamentally different strengthening mechanisms.

5.3.4 SXRD validation via L-PBF copper

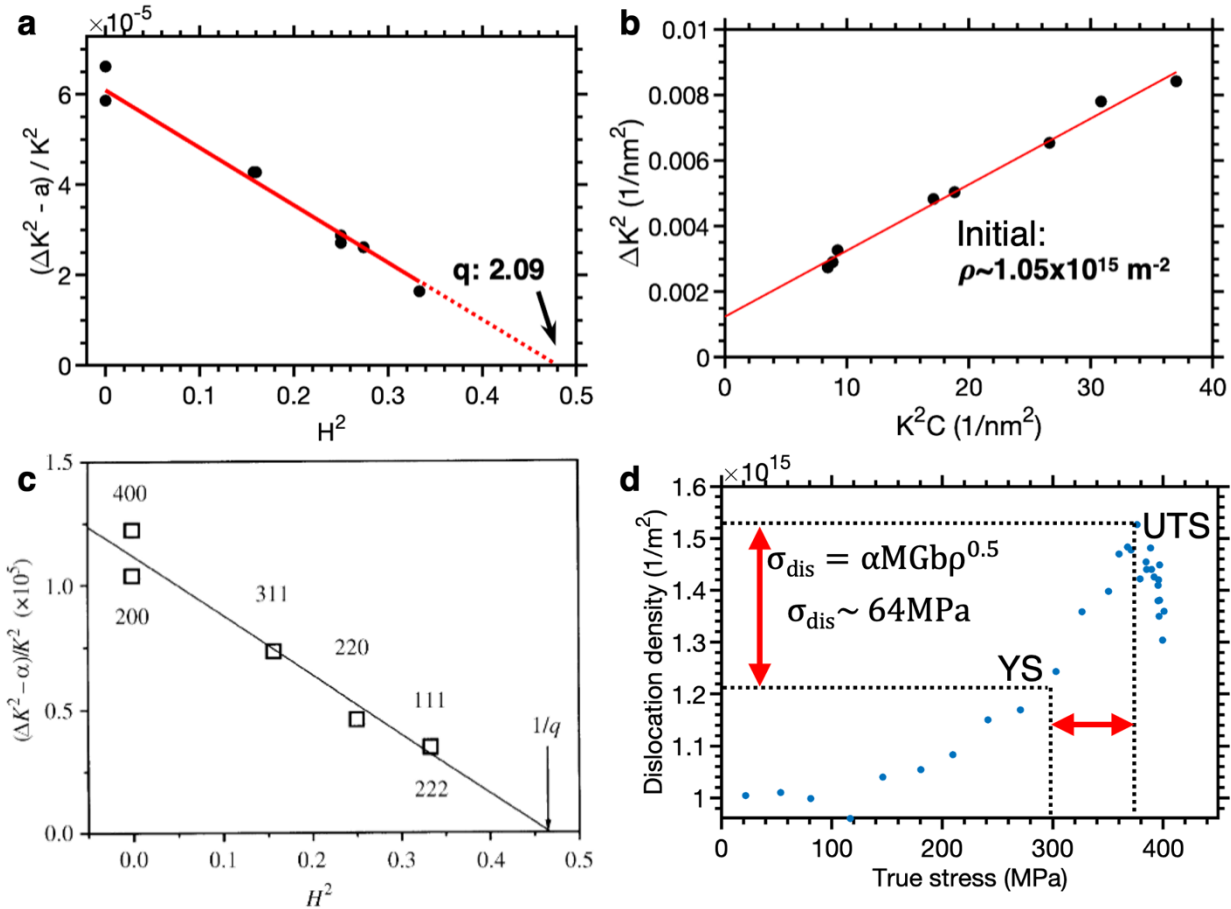


Figure 38 | m-WH plots used to quantify dislocation activity in AM Cu. **a** Linear regression extrapolation of q factor for the modified Williamson-Hall (m-WH) plot **b** Linear regression adjusted by contrast factor used to estimate dislocation density **c** Literature comparison of a pure

Cu system showing good agreement with the results in this work **d** Dislocation density evolution in additively manufactured (AM) Cu. The red vertical arrow shows the increase of dislocation density between yield strength (YS) and ultimate tensile strength (UTS), resulting in a dislocation hardening of ~64 MPa. The horizontal arrow shows the microscopic strengthening effect (~70 MPa), in good agreement with the calculated value.

L-PBF copper was chosen as a model system for validating SXRD peak-broadening analysis under mechanical loading. Its single-phase FCC structure and limited stacking-fault activity (Figure 37) suggest that deformation is dominated by dislocation activity. This AM Cu exhibits only a very small 111/222 strain divergence, which confirms that broadening changes can be attributed almost exclusively to dislocation storage rather than planar-fault formation or precipitate interactions.

This clarity is reflected directly in the m-WH analysis. Figure 38a-b presents two sets of linear regressions: the first allows extraction of the character parameter q , and the second yields the initial dislocation density. The q -fit trends match remarkably well with detailed studies reported in the literature for pure Cu (Figure 38c)—in both overall slope and extrapolated q factor [124,128]. The strong overlap with the literature provides quantitative confidence that the contrast-factor and m-WH formalism is correctly implemented here.

Figure 38d plots the dislocation density evolution throughout the tensile test for the AM Cu. The measured density over true stress relationship follows a monotonic increase in the post-yield regime (and before necking) scattering minimally — as expected in an alloy where hardening is governed by dislocation–dislocation interactions. Importantly, inserting the dislocation increase value between YS and ultimate tensile stress (UTS) into the Taylor hardening relation, shown in Figure 38d, produces a predicted strengthening increment that closely matches the measured work-

hardening increase at the macro-scale. The similarity between SXRD-derived defect evolution and mechanical response confirms that the m-WH analysis captures the dominant hardening mechanism with little ambiguity.

By demonstrating that dislocation-based broadening in a well-understood FCC metal reproduces both literature benchmarks and macroscopic strengthening trends, we establish a calibrated analytical foundation that serves as the basis for more complex analyses in FCC systems.

5.4 Summary

This chapter demonstrated how in-situ SXRD provides a unified framework for quantifying deformation mechanisms of FCC metals, beginning with well-behaved reference systems and progressively introducing more anisotropic elastic properties and SFEs. By examining lattice-strain evolution, peak broadening, and texture evolutions simultaneously, SXRD reveals when, where, and how defects are generated and accommodated as tensile loading unfolds.

Pure Cu served as a calibration benchmark. With deformation governed almost entirely by perfect dislocations, the m-WH analysis matched strengthening increments predicted by Taylor hardening closely. Moreover, the extracted q trend aligned with the available literature data for Cu, establishing confidence in the integrity and physical interpretation of the SXRD methodology reported.

Building upon this foundation, the introduction of additional defect mechanisms clearly altered the SXRD signatures in the more complex FCC materials studied. The divergence between $\{111\}$ and $\{222\}$ lattice-strain trajectories emerged as a reliable indicator of SFP. A consistent progression — most pronounced in CoCrNi, followed by 316L, diminished in Cu, and negligible

in AA7075-HIP — mirrored the well-established ordering of their respective SFEs. These results demonstrate that SXRD peak-position data can capture the onset of fault-mediated deformation, and that interpretation requires careful consideration of intrinsic material properties.

AA7075-HIP provided a contrasting example where deformation is shaped not by planar faults, but by a microstructure composed of TiC-stabilized fine grains and GB η precipitate cage structures. Here, lattice-strain evolution was comparatively isotropic across matrix reflections; however, combined with texture data and polar representations, spatial redistribution of grain families and their elastic response was still found to have a strong relation to the LD. These azimuthal measurements show that reliance on a single direction can be misleading, and that full-angular SXRD enables a richer mechanistic picture capable of supporting physically informed deformation modeling.

In summary, these findings underscore the versatility of in-situ SXRD, highlighting its ability to quantify and predict dislocation-mediated deformation, detect and quantify SFP, expose load partitioning between multiple phases and crystallographic orientations, and account for the orientation dependence of the deforming materials relative to LD. This chapter therefore establishes not only how SXRD captures deformation, but how it must be interpreted differently from one FCC alloy to another. These insights define a path toward physics-informed analysis of AM alloys, where SXRD serves as a critical tool for linking defect evolution to macroscopic performance with increasing predictive capability.

5.5 Future work

While Chapter 5 demonstrated the utility of SXRD for monitoring deformation mechanisms in additively manufactured FCC metals, several paths remain to expand the technique from qualitative comparison to predictive mechanistic modeling.

First, the alloy-specific interpretation of lattice strain deviation must be complemented by more explicit knowledge of slip system activation, ideally leveraging polycrystal plasticity simulations to identify the active slip systems in each material.

Second, extending the 180° azimuthal mapping beyond qualitative visualization requires linking directional strain evolution to intragranular constraint and grain-interaction hardening. These measurements provide a rich dataset suited for calibrating crystal-plasticity finite-element (CPFE) models of AM microstructures. Doing so may enable prediction not only of lattice-strain directionality but also of grain rotation rates, and the emergence of texture during plastic flow.

Third, while SFP estimates were inferred here from the divergence of 111/222 lattice strain, a more complete quantification will require combined peak-profile modeling — incorporating both shift and broadening behavior.

Finally, introducing temperature and strain-rate effects into the in-situ SXRD setup would help map when and how deformation transitions between slip-, fault-, and twinning-dominated regimes. Such data would establish general rules for interpreting SXRD responses in AM FCC alloys.

Chapter 6. Summary and future work

6.1 Summary

Additive manufacturing (AM) continues to expand alloy design possibilities by enabling solidification control and microstructural hierarchies unattainable by conventional processing. This dissertation advances both the development of new high-performance AM metals and the mechanistic interpretation of their deformation using in-situ synchrotron X-ray diffraction (SXRD), complemented by electron microscopy. Across face centered cubic (FCC) alloy systems, the work establishes how SXRD signatures must be interpreted in the context of alloy-specific deformation mechanisms to meaningfully connect structure and performance.

Laser powder-bed-fusion (L-PBF) of tungsten–boron alloys demonstrated that solidification-pathway modification can overcome long-standing printability barriers in refractory metals. A minor boron addition (0.3 wt.%) suppressed solidification cracking while simultaneously improving grain-boundary cohesion and reducing oxide formation — two critical enablers of plastic strain accommodation. These effects produced a near-fully dense, crack-free AM W alloy exhibiting tensile ductility at 800 °C, defining a pathway for deploying refractory metals for fusion and extreme-environment applications.

To develop a quantitative SXRD interpretation framework, this work then examined simple FCC model metals. Pure AM Cu served as a mechanistically “clean” system; because its stacking-fault probability (SFP) was observed to be low, plasticity is dominated by dislocation motion. Modified Williamson–Hall (m-WH) broadening analysis yielded dislocation densities and strengthening increments that matched Taylor hardening predictions and closely reflected

established trends in the literature. Thus, Cu validated SXRd-based defect quantification in a system where dislocation storage is the primary mechanism.

SXRd was subsequently extended to more complex FCC AM alloys — CoCrNi, 316L, and AA7075 — revealing deformation pathways increasingly influenced by microstructural hierarchy. Lattice-strain separation between $\{111\}$ and $\{222\}$ reflections tracked stacking-fault activity, with increasing divergence observed in CoCrNi - 316L - Cu - AA7075, proportional to expected stacking-fault energies (SFE). These results confirm that SXRd interpretation in AM alloys must reflect the active defect classes, not assume a universal peak-evolution model.

Building on these SXRd interpretation foundations, the TiC-inoculated Al-Zn-Mg-Cu alloy (AA7075) demonstrated how nanoparticle-assisted solidification and hierarchical precipitation can jointly produce exceptional strength–ductility performance. TiC nanoparticles not only refined grains and eliminated hot tearing during L-PBF, but also dictated the subsequent formation of a grain-boundary MgZn_2 “cage,” where large boundary precipitates and smaller GB features remain anchored at TiC-pinned interfaces. This cage strengthens the alloy even in the HIP condition, resolving a large portion of the strengthening previously unaccounted for in classical grain boundary and dislocation terms.

T6 aging then introduced a dense intragranular η' /cluster population, adding a complementary internal load-bearing network. In-situ SXRd peak-shift mapping provided direct mechanistic evidence of this redistribution: as tensile deformation progressed, load first transferred from matrix to GB cage (HIP), and then, in H6, was shared between GB η and intragranular η' , delaying localization and still enabling extensive work hardening. The coordinated evolution of

lattice strain, peak broadening, and diffraction intensity showed how TiC-stabilized boundaries and nanoscale obstacles together govern plasticity pathways.

The outcome is a rare strength–ductility synergy: the highest specific ultimate tensile strength ever reported for a 7xxx series aluminum alloy, exceeding even that of conventionally processed Ti-6Al-4V, while retaining substantial ductility. Crucially, AA7075 reveals that precipitation strengthening must be interpreted holistically: the GB cage contributes significantly to the total strengthening, with η' supplying the incremental hardening necessary to shift plasticity into the grain interior rather than concentrating it at boundaries.

6.2 Future Work

The results of this dissertation reveal that mechanical performance in AM structural alloys depends as much on how microstructures are engineered during solidification as on their nominal chemistry. Future efforts should extend these mechanistic insights into predictive design strategies.

For W-B alloys, high-temperature in-situ SXRD or neutron diffraction should quantify how boride dispersion and grain-boundary chemistry sustain plasticity at more extreme fusion-relevant temperatures and under irradiation. These studies will refine alloying and processing routes to maximize the already demonstrated combination of strength and high-temperature ductility.

For TiC-inoculated AA7075, systematic variations in nanoparticle volume fraction, size, and matrix compatibility could fine-tune both grain refinement and the balance between GB η “cage” strengthening and η' -mediated intragranular deformation. High-temperature SXRD should establish the thermal limits of the cage-mediated load-sharing transition and its role in preserving ductility despite very high strength.

More broadly, SXRD-based mechanistic inputs—including defect evolution, load partitioning, and residual stress storage—should be integrated into microstructure-informed constitutive modeling and AM process-development. Doing so will allow SXRD to shift from a diagnostic technique to a predictive tool for alloy design.

Finally, these strategies should be extended to additional AM alloy classes (HCP systems, oxide-strengthened steels, refractory alloys beyond W-B), potentially enabling deformation pathways unattainable through conventional processing. Through such work, solidification engineering and in-situ characterization can jointly drive the development of structural materials once considered beyond reach.

Appendix A: Glossary

AA7075 / 7075: Al-Zn-Mg-Cu alloy

AM: Additive Manufacturing

AP: As-Printed

BCC: Body-Centered Cubic

BD: Build Direction

BF-STEM: Bright-Field Scanning Transmission Electron Microscopy

BF: Bright-Field (microscopy)

B-W: Boron–Tungsten binary system

BSE: Back-Scattered Electrons

CAD: Computer-Aided Design

CBED: Convergent Beam Electron Diffraction

CHESS: Cornell High Energy Synchrotron Source

CNC: Computer Numerical Control

DBTT: Ductile-to-Brittle Transition Temperature

DF: Dark-Field (microscopy)

EBM: Electron Beam Melting

EBSD: Electron Backscatter Diffraction

EDM: Electrical Discharge Machining

EDS: Energy-Dispersive X-ray Spectroscopy

FCC: Face-Centered Cubic

FIB: Focused Ion Beam

FWHM: Full Width at Half Maximum

GP Zones: Guinier-Preston Zones

HIP: Hot Isostatic Pressing

HREBSD: High-Resolution EBSD

HRTEM: High-Resolution Transmission Electron Microscopy

HT: Heat-Treated / Heat Treatment (context-dependent)

ICME: Integrated Computational Materials Engineering

L-PBF / LPBF: Laser Powder-Bed-Fusion

LD: Loading Direction

NTR: Near-Theoretical Density (printing context)

PFZ: Precipitation-Free Zone

RT: Room Temperature

SAXS: Small-Angle X-ray Scattering

SE: Secondary Electrons

SEM: Scanning Electron Microscopy

SFE: Stacking Fault Energy

SS: Solid Solution

STEM: Scanning Transmission Electron Microscopy

STL: Stereolithography (mesh file format)

SUTS: Specific Ultimate Tensile Strength

SVE: Standard Video Extensometer

SXRD: Synchrotron X-ray Diffraction

TD: Transverse Direction

TEM: Transmission Electron Microscopy

TKD: Transmission Kikuchi Diffraction

UE: Uniform Elongation

UTS: Ultimate Tensile Strength

WA / W-A: Warren–Averbach (peak broadening analysis)

XRD: X-ray Diffraction

YS: Yield Strength

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