Snapshot Reviews in Emerging Fields

Control of grain structure, phases, and defects in additive manufacturing of high-performance metallic components

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Cracking

ABSTRACT

The properties and serviceability of 3D-printed metal parts depend on a variety of attributes. These include the chemical composition, phases, morphology, spatial distributions of grain size and shape, crystallographic texture, and various defects. Control of these attributes remains an exciting opportunity and a major challenge because of the many process variants and parameters that need to be optimized. The desired attributes of industrially relevant common additive manufacturing alloys such as steels, nickel, titanium, aluminum, and copper alloys, and functionally graded materials vary widely and require alloy-specific strategies for their control. The recent reviews address the valuable processing-microstructure-property relations but do not focus on their control strategies. Here we seek to unify the disjointed literature and critically review recent advances in controlling grain structure, phases, and defects. The emerging use of digital tools such as mechanistic models and data-driven techniques such as machine learning, dimensional analysis, and statistical methods in controlling part attributes is emphasized. Finally, we identify opportunities for high-impact research in metal printing and present an outlook for the future based on existing evidence.

1. Introduction

Additive manufacturing (AM) is attractive because of its ability to produce unique components that cannot be made by more established conventional technologies [1–6]. Production of parts with intricate geometry such as components with internal cooling channels, the substitution of an assembly of many parts with one integrated design such as the fuel nozzle for jet engines, and the flexibility of a single machine to make a variety of parts are some of its attractions [7–15]. However, its market penetration has been tempered by quality consistency issues, specifically the inability to adequately control microstructural features that limit the performance of the parts without post-processing [2]. Its cost competitiveness and acceptability during the part qualification process are related to the chemical composition, phases, morphology, spatial distributions of grain size and shape, crystallographic texture, and

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Various defects that define the microstructures, properties, and serviceability of additively manufactured metallic parts [1, 3]. Since there are many process variants and process variables, control of these attributes remains a major challenge to optimize microstructures and properties [1]. The desired grain structures, phases, and defects of industrially relevant common additive manufacturing alloys such as steels, nickel, titanium, aluminum, and copper alloys, and functionally graded materials are unique (Table 1.1) and require alloy-specific strategies for their control. Unlike in welding and casting, optimizing these attributes by trial and error is not a viable path because of the high cost of equipment and feedstock, and the need to cover the large process parameter space for metal printing [3].

An increasing number of publications and several reviews [16–23] on the microstructure and defect control of AM parts are available in the literature. Since AM is rapidly evolving and innovations are constantly developed, a periodic critical assessment of our understanding is necessary and this review seeks to fulfill this need. What is needed and not currently available are the specific roadmaps for the control of the most important microstructural features of the widely used alloy systems for metal printing to make parts with minimum defects and optimum microstructures. The large volume of individual papers and recent reviews address the valuable processing-microstructure-property relations qualitatively but do not focus on the control strategies of the important microstructural attributes. This is an area where the synthesis of emerging digital tools [1, 4] and the available information on the characterization of additively manufactured materials can provide a useful pathway for engineers to adopt an expeditious route for

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Grain structures</th>
<th>Phases</th>
<th>Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic stainless steels</td>
<td>Solidification mode depends on the Ni and Cr equivalents</td>
<td>Microsegregation in the intercellular regions results in Cr and Mo enrichment which stabilize ferrite</td>
<td>Lack of fusion and porosity are often observed</td>
</tr>
<tr>
<td></td>
<td>Solidifies primarily in either ferrite-austenite or austenite mode</td>
<td>Generally, no martensite formation</td>
<td>Mn and Cr are susceptible to vaporization</td>
</tr>
<tr>
<td></td>
<td>The microstructure can be columnar or equiaxed or a mixture of both</td>
<td>Nanoscale oxide inclusions are often observed</td>
<td>Stress corrosion cracking is observed</td>
</tr>
<tr>
<td>Martensitic steels</td>
<td>Primarily exhibit cellular or dendritic grain structure</td>
<td>Tool steels, low alloy steels, and ferritic-martensitic steels form martensite and Cr, V, W, and Mo rich carbides</td>
<td>Lack of fusion, gas porosity, and keyhole porosity are common</td>
</tr>
<tr>
<td></td>
<td>Grains grow primarily along the preferential (001) solidification direction</td>
<td>Maraging steels form Ni3Mo and Ni3(Ti, Al) precipitates along with martensite,Cr</td>
<td>Mn and Cr are the most susceptible element to the vaporization</td>
</tr>
<tr>
<td></td>
<td>Grain size varies widely depending on the cooling rates</td>
<td>in maraging steels does not precipitate but raises the martensite start temperature</td>
<td>Solidification cracking is often observed</td>
</tr>
<tr>
<td>Duplex steels</td>
<td>A high concentration of Cr stabilizes the primary β-ferrite and austenite forms from ferrite</td>
<td>Brittle sigma phases are often observed</td>
<td>Lack of fusion, gas porosity, keyhole porosity, and composition change are often observed</td>
</tr>
<tr>
<td></td>
<td>Grain boundary austenite, Widmanstatten austenite, intragranular austenite, and secondary austenite morphologies</td>
<td>Nitride inclusions form at the grain boundaries depending on the nitrogen content</td>
<td>Less susceptible to cracking than other steels</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>Long columnar grains often cause anisotropic tensile properties</td>
<td>Si and Fe rich precipitates are often found within the primary α grains</td>
<td>Solidification cracking and liquation cracking are major issues</td>
</tr>
<tr>
<td></td>
<td>Grain refiners and inoculants are often added to achieve equiaxed grains</td>
<td>Precipitation-strengthened alloys are often heat treated to achieve desired phases and properties</td>
<td>Mg and Zn may selectively vaporize</td>
</tr>
<tr>
<td></td>
<td>Dendritic arm spacing vary significantly depending on the cooling rates</td>
<td>Segregation of Nb, Mo, Al, Ta, and C in the interdendritic region forms carbides and laves phases-Strengthening precipitates (γ' and γ)</td>
<td>Lack of fusion and gas porosities are also observed</td>
</tr>
<tr>
<td></td>
<td>Single crystals with no grain boundaries are also printed</td>
<td>are formed in as-deposited as well as heat-treated samples and affect properties</td>
<td>Solidification cracking, liquation cracking, ductility dip cracking, and strain age cracking are common</td>
</tr>
<tr>
<td></td>
<td>Grain refiners are often added to form small equiaxed grains to improve mechanical properties</td>
<td></td>
<td>Susceptible to Cr vaporization loss</td>
</tr>
<tr>
<td></td>
<td>The formation of stray grains often affects single crystalinity</td>
<td></td>
<td>Lack of fusion, gas porosities, and keyhole porosities are often found</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>β grains (BCC) form after solidification followed by α grains (HCP) within the prior β grains below the β transus temperature</td>
<td>The volume fraction of α phases depends on α stabilizing elements such as Al, N, C, and O</td>
<td>Very sensitive to the pickup of C, N, O, and H from the atmosphere</td>
</tr>
<tr>
<td></td>
<td>β grains are long and columnar and α grains are small with dispersed and basketweave structure</td>
<td>α’ martensite (HCP) is often formed at high cooling rates An orthorhombic α’ structure is observed depending on the amount of V, Cr, and Nb</td>
<td>Lack of fusion, gas porosity, keyhole porosity, and composition change are often found</td>
</tr>
<tr>
<td></td>
<td>Single phase β-grain structure is observed for metastable β alloys</td>
<td>(β stabilizer)</td>
<td>Generally do not crack</td>
</tr>
<tr>
<td>Copper alloys</td>
<td>Columnar and equiaxed dendrites are observed depending on process parameters and composition</td>
<td>Form grain boundary precipitates rich with Cr, Zr, Ti, and Ni</td>
<td>Alloying element segregation causes cracking</td>
</tr>
<tr>
<td></td>
<td>Printed bronze parts show long grains aligned along the build direction</td>
<td>The shape and size of precipitates affect the toughness of parts</td>
<td>Lack of fusion and gas porosities are common</td>
</tr>
</tbody>
</table>
advancing additive manufacturing by improving part quality based on scientific principles.

Control of solidification structure, grain structure, phase composition, and defects for each commonly used alloy system aided by the valuable and growing characterization literature and synthesized with powerful physics-based and data-driven techniques can impact all steps of AM technology [1]. There is a growing consensus that the technology of AM will not mature following the same path followed by the traditional established manufacturing technology such as welding and casting [1,3]. The advantages achievable by using emerging powerful digital tools such as mechanistic modeling, machine learning, and digital twins provide a more scientific and expeditious route for the development of AM than that achieved before for the other manufacturing technologies [4]. While there is growing literature on the characterization of metallic components, the papers focus on various alloys, AM processes, and process variables. The results show that there is no definitive single pathway for the control of grain structure, phases, and defects. Encompassing all aspects of AM including product design, process planning, production monitoring and control, control of microstructural features and defects, inspection, and qualification, digital tools can significantly reduce trial and error testing and part rejection, improve quality and reduce cost [1]. We seek to synthesize existing literature to provide a roadmap for each commonly used AM alloy

Fig. 2.1. (a) A schematic diagram of a solidification map showing grain morphology variation for different values of temperature gradient and solidification growth rate [32]. (b-c) Computed grain structures at two longitudinal vertical planes during DED-L of Inconel 718 showing smaller grain size away from the mid-section [36], (b) 240 µm from the central plane and (c) 840 µm from the mid-plane.
system for engineers to use as a practical guide based on scientific principles.

Here we critically review recent advances for controlling grain structure, phases, and defects based on experiments, mechanistic modeling, machine learning, and other data-driven techniques. We uncover the alloy-specific control strategies to achieve the desired microstructures in various types of steels, aluminum, nickel, titanium, and copper alloys, and functionally graded materials produced by powder bed fusion with laser (PBF-L) and electron beam (PBF-EB) as well as directed energy deposition with laser (DED-L), electron beam (DED-EB), gas metal arc (DED-GMA), and plasma arc (DED-PA). These alloys are selected based on their importance in additively manufactured parts. We review the scientific foundation for the manufacture and repair of single crystal parts that are potentially attractive to aerospace and other industries. We also address the important need for the control strategies of common defects and review the emerging use of mechanistic models and data-driven techniques in controlling part attributes. Finally, we identify opportunities for high-impact research and present an outlook for the future based on evidence.

2. Theories of grain structures, phases, and defects formation

2.1. Grain structure

Solidification morphology and grain size are the two most important attributes of grain structure [24–29] because they affect the properties and serviceability of additively manufactured metallic parts. Theories of the evolution of grain morphology and size distribution in additive manufacturing have benefitted from the rich knowledge base of metallurgy and fusion welding where the scientific principles of grain growth have been a subject of considerable interest for many decades.

2.1.1. Grain morphology

The liquid needs to be cooled below the liquidus temperature for the growth of a solid. The extent of undercooling [30], defined as the difference between the liquidus temperature and the liquid’s local temperature, is the sum of contributions from solute undercooling ($\Delta T_C$), curvature undercooling ($\Delta T_R$), thermal undercooling ($\Delta T_T$), and kinetic undercooling ($\Delta T_K$):

$$\Delta T = \Delta T_C + \Delta T_R + \Delta T_T + \Delta T_K$$

(1)

The undercooling affects the evolution of microstructure, particularly the morphology of the solidification front and the phase selection. For example, Hunt [31] suggested that equiaxed growth would occur when the temperature gradient, $G$, is less than that given by the following expression:

$$G < 0.617 N_0^{1/4} \Delta T_C \left(1 - \frac{\Delta T_K}{\Delta T_C^2}\right)$$

(2)

where $N_0$ is nucleant density ($1/m^3$), $\Delta T_C$ represents solute undercooling of dendrite tip ($K$) and $\Delta T_R$ represents undercooling for heterogeneous nucleation which is typically small. While the morphology has been correlated with the undercooling using elegant theories, the applications of these theories require values of parameters such as $N_0$ which cannot be accurately prescribed based on theory. Therefore, a usable framework that connects quantifiable parameters with morphology such as planar, cellular, or dendritic, is needed.

A commonly used methodology for estimating the morphology of a solidifying alloy is a plot of temperature gradient ($G$) versus solidification growth rate ($R$) [32] shown in Fig. 2.1 (a). The increase of $G/R$ results in morphology change from equiaxed, to dendritic to cellular to planar. During additive manufacturing, the ratio of $G/R$ is much lower than that required for planar solidification. In contrast, columnar dendritic morphology which is susceptible to cracking is often observed. Processing conditions and alloy composition determine the temperature field and the local solidification growth rate at various locations. The parameters, G and R are often controlled to achieve solidification conditions favorable for equiaxed grain formation. A low value for the temperature gradient to solidification rate ratio ($G/R$ ratio) at the liquid/solid interface needs to be achieved to obtain equiaxed microstructure [25].

Heat source power, scanning speed, scanning pattern, beam radius, power distribution, preheating temperature, and other variables may be adjusted to achieve favorable G and R. A well-tested heat transfer and fluid flow model can provide reliable values of temperature field and solidification growth rates at various locations in the three-dimensional space. In addition, grain refiners and inoculants are often added to promote heterogeneous nucleation within the liquid to achieve equiaxed grains [26]. External agitations such as ultrasonic vibrations have also been used to break the long columnar grain during AM [27]. These techniques of controlling the morphologies are reviewed for different alloy systems in Section 3 of this review.

2.1.2. Grain size

Grain size controls the mechanical properties of parts such as hardness, yield strength, and creep life. Since grain growth depends on time–temperature history, the grain size can vary spatially depending on the local variation in temperature with time [29]. As a result, theories of grain size evolution have been of much interest in metallurgy. One of the first theories of grain growth was proposed by Burke and Turnbull [33] who assumed that the grain boundary velocity was inversely proportional to its radius of curvature, and showed the following parabolic kinetics for grain growth:

$$R_t^2 - R_0^2 = Kt$$

(3)

where $R_0$ and $R_t$ are the average radii of grains at times zero and $t$, and $K$ is a constant. Since the diffusion of atoms across a grain boundary is considered to be an activated process, it can be shown that the constant $K$ can be replaced by the following expression:
where \( K_0 \) is a constant, \( Q \) is the activation energy for diffusion and \( T \) is the temperature. Thus, equation (4) indicates faster grain growth at higher temperatures. However, since grains are surrounded by other grains, they cannot be treated as isolated entities. Both the driving forces for the migration of boundaries and the topological considerations need to be considered for grain growth. Since the parabolic grain growth model, several other analytical models have been proposed to overcome its deficiencies [34]. However, the complexity of grain size variations in three dimensions in non-isothermal systems has not been modeled by analytical models. In addition, the spatial gradient of temperatures also imposes “thermal pinning” [35] which cannot be predicted by analytical calculations. Therefore, numerical models such as Monte Carlo simulations have been proposed considering grains as a topologically connected network in a three-dimensional space where significant variations of temperature exist [36].

Rapid cooling at low heat input results in smaller grains. Since different AM processes use significantly diverse heat inputs (Table 2.1), they exhibit a striking difference in grain size. For example, AlSi10Mg parts printed using PBF-L [37] using 0.28 to 0.41 J/mm heat input exhibit significantly finer grain size (0.53 to 0.93 \( \mu \text{m} \)) than those produced using DED-L (48 \( \mu \text{m} \)) [38] where the heat input is 100 J/mm (Table 2.1). Schneider et al. [28] compared the grain size of Inconel 718 parts printed using DED-L, DED-GMA, and PBF-L. The lowest heat input in PBF-L resulted in rapid cooling and fine grains [28]. For the same heat input, Fig. 2.1 (b) and (c) compare grain growth during DED-L of Inconel 718 in two vertical longitudinal planes. The plane considered in (b) was 240 \( \mu \text{m} \) from the central vertical plane and the plane (c) was 840 \( \mu \text{m} \) from the central vertical plane. Temperatures are lower further away from the middle planes and as a result, the grain size in plane (c) was much smaller than the average grain size in the plane (b).

Table 2.1 provides several examples [36–52] of the variations in solidification morphologies and grain size in different alloy parts printed using various AM processes. Grain size can be controlled by adjusting the cooling rates by varying the processing conditions and by employing post-process heat treatment as explained in Section 3 of the review.

### 2.2. Phases

The evolution of grain structure, as discussed in the previous section, is a critical step in the formation of the microstructure of a metal AM part. However, after the metal has solidified and cooled below its solidus temperature, it must still cool to room temperature and can go through phase transformations along the way [53–56]. These transformations result in a wide variety of primary and secondary phases with diverse crystal structures and chemical compositions as summarized in Table 2.2. These phases significantly affect the microstructure and mechanical properties of parts [16,57]. The theories behind the formation of these phases are reviewed below.

#### 2.2.1. Phase diagrams and constitution diagrams

Phase diagrams [58,59] are widely used for understanding the phase composition of an alloy of known chemical composition at a given temperature under equilibrium. For many systems, the phase transformations are time-dependent, and phase diagrams provide...
A wide variety of phases with diverse crystal structures and chemical compositions formed in steels and alloys of aluminum, nickel, and titanium.

<table>
<thead>
<tr>
<th>Phase in C-Mn Steels</th>
<th>Symbol</th>
<th>Crystal Structure</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Ferrite</td>
<td>α</td>
<td>BCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Austenite</td>
<td>γ</td>
<td>FCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Delta Ferrite</td>
<td>δ</td>
<td>BCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Cementite</td>
<td>θ (Fe₃C)</td>
<td>Orthorhombic</td>
<td>Iron carbide</td>
</tr>
<tr>
<td>Epsilon Carbide</td>
<td>ε (Fe₄C)</td>
<td>Hexagonal</td>
<td>Transition Carbide</td>
</tr>
<tr>
<td>Eta Carbide</td>
<td>η (Fe₅C)</td>
<td>Orthorhombic</td>
<td>Transition Carbide</td>
</tr>
<tr>
<td>Martensite</td>
<td>α'</td>
<td>Tетragonal</td>
<td>Non-Equilibrium phase</td>
</tr>
<tr>
<td>Bainite</td>
<td>α₈₀, α₉₀</td>
<td>BCC + Carbides</td>
<td>Non-Equilibrium phase</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phases in Alloys Steels</th>
<th>Symbol</th>
<th>Crystal Structure</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Ferrite</td>
<td>α</td>
<td>BCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Austenite</td>
<td>γ</td>
<td>FCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Delta Ferrite</td>
<td>δ</td>
<td>BCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Alloy Carbide</td>
<td>MC</td>
<td>FCC</td>
<td>M = Ti, Nb, V, Ta, W</td>
</tr>
<tr>
<td>Alloy Carbide</td>
<td>M₃C₆</td>
<td>FCC</td>
<td>M = Cr, Mo, Fe</td>
</tr>
<tr>
<td>Alloy Carbide</td>
<td>M₅C₇</td>
<td>Hexagonal</td>
<td>M: multiple elements</td>
</tr>
<tr>
<td>Martensite</td>
<td>α'</td>
<td>Tетragonal</td>
<td>Non-Equilibrium phase</td>
</tr>
<tr>
<td>Pearlite</td>
<td>P</td>
<td>BCC + Carbides</td>
<td>Ferrite + Carbide Constituents</td>
</tr>
<tr>
<td>Bainite</td>
<td>α₈₀, α₉₀</td>
<td>BCC + Carbides</td>
<td>Ferrite + Carbide Constituents</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phases in Ni Alloys</th>
<th>Symbol</th>
<th>Crystal Structure</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma</td>
<td>γ</td>
<td>FCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Gamma prime</td>
<td>γ'</td>
<td>L12</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Delta</td>
<td>δ</td>
<td>FCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Sigma</td>
<td>σ</td>
<td>Orthorhombic</td>
<td>Non-Equilibrium</td>
</tr>
<tr>
<td>Laves phases</td>
<td>NiₓX₀</td>
<td>L12</td>
<td>X = Cr, Mo, Fe</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phases in Ti Alloys</th>
<th>Symbol</th>
<th>Crystal Structure</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha</td>
<td>α</td>
<td>Hexagonal</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Beta</td>
<td>β</td>
<td>BCC</td>
<td>Equilibrium phase</td>
</tr>
<tr>
<td>Alpha Prime</td>
<td>α'</td>
<td>HCP</td>
<td>Martensitic phase</td>
</tr>
<tr>
<td>Alpha Double Prime</td>
<td>α''</td>
<td>Orthorhombic</td>
<td>Martensitic phase</td>
</tr>
<tr>
<td>Omega</td>
<td>ω</td>
<td>Hexagonal</td>
<td>Metastable phase</td>
</tr>
</tbody>
</table>

The state of the system after a long time when equilibrium is attained. A phase diagram is a graphical representation of the relationships between the various phases of a material at different temperatures, pressures, and compositions. It shows the conditions under which different phases exist and their stability ranges. By using phase diagrams, scientists and engineers can predict which phases will form during the additive manufacturing process [58,59]. Apart from the primary phases such as austenite and ferrite in steels, phase diagrams can include secondary phases such as carbides, nitrides, oxides, intermetallic compounds, and martensite [16,57]. Table 2.3 provides several examples [60–91] of such phases in different alloy parts printed using various AM processes. These phases significantly affect the mechanical properties of parts [16,57]. For example, Laves phases are intermetallic compounds formed during AM of nickel-base superalloys and are known to degrade the toughness of parts [57].

Constitution diagrams such as the Schaeffler diagram (Fig. 2.2 (a)) for stainless steels are useful tools for understanding the phase formation during additive manufacturing [92,93]. It is a graphical representation of the chemical composition of stainless steel, which helps to predict the austenitic, ferritic, or martensitic phase formation [92,93]. The diagram considers the effects of both alloying elements and thermal history on the formation of the phases. During additive manufacturing, stainless steel undergoes rapid heating and cooling, leading to complex phase transformations. By using the Schaeffler diagram, it is possible to predict the final microstructure of the material based on the initial chemical composition, processing conditions, and cooling rates [92,93].

2.2.2. Johnson–Mehl–Avrami–Kolmogorov equation

The Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation [52,94,95] is a mathematical model used to describe the kinetics of phase transformations in materials. The JMAK equation relates the volume fraction of transformed material to time and temperature, taking into account the nucleation and growth of new phases. The JMAK equation is given by [52,95]:

\[
V = 1 - \exp\left[-(kt)^n\right]
\]  

where \( V \) is the volume fraction of the new phase, \( k \) is the rate constant, \( t \) is time, and \( n \) is the Avrami exponent, which is related to the dimensionality of the growth process. The JMAK equation assumes that the phase transformation proceeds by nucleation and growth and that the growth rate is proportional to the volume fraction of the new phase. The Avrami exponent can take values between 1 and 4, depending on the geometry of the growing phase and the reaction mechanism [52,95]. By fitting experimental data to the
transformation approaches completion, there is minimal untransformed material for nucleation, resulting in a slowdown in the pro-
nuclei develop into particles and consume the old phase while new nuclei continue to form in the remaining parent phase. As the
due to the time it takes for a significant number of nuclei to form and grow. In the intermediate period, transformation is fast as the
transformation by sliding of \(\{111\}\) planes over one another of FCC structure.

- For example, a face-centered cubic structure can be transformed into a hexagonal close-packed structure by the Martensitic
transformations that involve the displacement of a large number of atoms by a small distance such as a small fraction of the interatomic

Table 2.3

<table>
<thead>
<tr>
<th>Phases</th>
<th>Alloys</th>
<th>AM process</th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbidies</td>
<td>Stainless steel 316</td>
<td>PBF-L</td>
<td>Nano-scale carbides such as Mn(_2)C(_2) are formed</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>15-5 PH stainless steel</td>
<td>PBF-L</td>
<td>Fine, nano-scale carbide precipitates</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td>9Cr-1Mo steel</td>
<td>PBF-L</td>
<td>Precipitation of Mn(_2)C(_2) carbide</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>Inconel 718</td>
<td>PBF-L</td>
<td>Primarily (Nb, Ti)C carbides are observed</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>Inconel 625</td>
<td>DED-L</td>
<td>Cr(_{23})C(_6) and NiC are formed</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>Inconel 718</td>
<td>DED-GMA</td>
<td>Carbides precipitate in the heat-affected zone</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td>Alloy 800H</td>
<td>PBF-L</td>
<td>Cr(_{23})C(_6) and Cr(_3)C(_2) are formed</td>
<td>[66]</td>
</tr>
<tr>
<td></td>
<td>Haynes 282 superalloy</td>
<td>DED-L</td>
<td>Globular, nano-sized Ti and Mo-rich carbides of MC and Mo(_2)C(_6) are</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>Ti-3Al-8 V-6Cr-4Mo-4Zr alloy</td>
<td>DED-GMA</td>
<td>(Ti, Mo)C and (Cr,Mn,Mo)(_{23})C(_6) precipitate</td>
<td>[68]</td>
</tr>
<tr>
<td>Nitrides</td>
<td>Inconel 718</td>
<td>PBF-L</td>
<td>Micro-sized, irregular-shaped, Ti-rich nitrides</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>Duplex steel 2507</td>
<td>DED-GMA</td>
<td>Cr-rich nitrides precipitate in the heat-affected zone</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>2205 duplex stainless steel</td>
<td>DED-GMA</td>
<td>Mainly Cr-rich nitrides form near the fusion boundary</td>
<td>[72]</td>
</tr>
<tr>
<td>Oxides</td>
<td>Stainless steel 316</td>
<td>PBF-L</td>
<td>Oxides of Cr and Mn</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>Stainless steel 316</td>
<td>DED-L</td>
<td>Oxides of Cr and Mn</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Stainless steel 316</td>
<td>PBF-L</td>
<td>Depending on the oxygen concentration (Mn, Cr)Cr(_2)O(_4), SiO(_2), and Cr(_3)O(_5) are</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>17-4 PH steel</td>
<td>DED-PA</td>
<td>Micron-scale layers of Cr(_2)O(_3) are formed</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>Maraging Steel M789</td>
<td>PBF-L</td>
<td>TiO(_2) and Al(_2)O(_3) are formed</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td>Commercially pure Cu</td>
<td>PBF-L</td>
<td>Cu(_6)O and CuO(_2) precipitate of 2 to 30 nm size are formed</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>Stainless steel 316</td>
<td>PBF-L</td>
<td>Nano-sized MnSiO(_3) is formed</td>
<td>[79]</td>
</tr>
<tr>
<td>Intermetallic compounds</td>
<td>Inconel 738LC</td>
<td>DED-GMA</td>
<td>Ni(_3)(Al,Ti) intermetallic compounds are formed</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>Al-Si alloy</td>
<td>DED-GMA</td>
<td>A short rod-like Fe-intermetallic compound was observed at the grain boundaries</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td>Inconel 718</td>
<td>DED-L</td>
<td>Laves phases are observed</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>Inconel 718</td>
<td>PBF-L</td>
<td>Discrete nano-scale Laves phase particles are formed</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>Inconel 718</td>
<td>DED-L</td>
<td>Laves phases significantly degrade the tensile properties</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>Inconel 718</td>
<td>DED-L</td>
<td>Laves phases of different sizes and morphologies are obtained</td>
<td>[84]</td>
</tr>
<tr>
<td>Martensite</td>
<td>18Ni maraging steel</td>
<td>PBF-L</td>
<td>Low carbon BCC martensite and FCC retained austenite crystal structures</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>Ti6242S alloy</td>
<td>PBF-L</td>
<td>Soft, orthorhombic martensite</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>Long laths of martensite</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>H13 tool steel</td>
<td>DED-GMA</td>
<td>Formation of martensite increased hardness</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>Fe-0.45C steel</td>
<td>PBF-L</td>
<td>Martensites are partially tempered due to repeated thermal cycles</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>Grade 91 ferritic steel</td>
<td>DED-L</td>
<td>The amount of martensite and tempered martensite affects the hardness variation</td>
<td>[91]</td>
</tr>
</tbody>
</table>

JMAK equation, researchers can extract the rate constant and the Avrami exponent, which provide insights into the kinetics of phase
formation during additive manufacturing processes [52,94]. Transformations typically exhibit an s-shaped, or sigmoidal profile where transformation rates are slow at the start and end of the process, but rapid in the middle (Fig. 2.2 (b)). The slow rate at the beginning is
due to the time it takes for a significant number of nuclei to form and grow. In the intermediate period, transformation is fast as the
nuclei develop into particles and consume the old phase while new nuclei continue to form in the remaining parent phase. As the transformation approaches completion, there is minimal untransformed material for nucleation, resulting in a slowdown in the production
of new particles. It is often applied to understand the phase formation that occurs during the additive manufacturing of
metallic materials [52,94].

2.2.3. TTT curves and CCT curves

At a given temperature, the extent of a given diffusion-controlled transformation depends on the time of transformation. Time-
temperature-transformation (TTT) diagrams or isothermal transformation diagrams show percentage transformation versus time at
a constant temperature. Plots of temperature versus time (latter in a logarithmic scale) show percentage completion curves for a certain
phase transformation (or reaction), in many cases the shape of these curves resembles that of “C” and is sometimes referred to as C-
curves. Although they are most commonly used for austenite decomposition during cooling in steels, they can also be used to describe
any phase transformations. For example, time–temperature-transformations diagrams are available for the growth and dissolution of
various types of inclusions such as oxide and nitride inclusions in steels. [96,97]. Most standard textbooks provide many examples of
TTT diagrams, most commonly for steels. For example, TTT diagrams for eutectoid steels show the transformations of austenite to
coarse pearlite and fine pearlite or bainite. They also show the occurrence of a diffusionless process that results in the formation of
martensite below the martensite start temperature when the specimens are cooled rapidly. Martensitic transformations are displacive
transformations that involve the displacement of a large number of atoms by a small distance such as a small fraction of the interatomic
spacing. For example, a face-centered cubic structure can be transformed into a hexagonal close-packed structure by the Martensitic
transformation by sliding of (111) planes over one another of FCC structure.

7
In additive manufacturing, phase transformations do not occur under isothermal conditions because of repetitious heating and cooling. TTT diagrams can be transformed to include continuous temperature changes, particularly cooling, and the modified diagrams that take this into account are called continuous cooling transformation diagrams or CCT diagrams. Depending on how the temperature changes with time, the time necessary to attain a certain transformation changes. During continuous cooling, the transformation resulting from the cooling shifts the constant % transformation curves downwards and to the right of the TTT curves for isothermal transformation.

2.3. Defects

Mechanical properties, quality, reliability, and serviceability of parts are often affected by common defects such as cracking, loss of alloying elements, lack of fusion, porosity due to gas bubbles, and keyhole instability-induced porosity (Table 2.4). The theories of the evolution of these defects are discussed below.

2.3.1. Solidification cracking

Solidification cracking [98–102] is common in additively manufactured parts of aluminum and nickel alloys and austenitic stainless steels. Since an alloy melts and solidifies over a range of temperatures, a mushy zone forms behind the molten pool, and a
partially melted zone exists in the region of the workpiece around the molten pool (Fig. 2.3 (a)). In the mushy zone, grains are typically columnar with intergranular liquid films (Fig. 2.3 (a)). This region has limited ductility and is unable to accommodate significant tensile deformation without cracking. Some areas adjacent to the fusion zone may also have limited ductility (Fig. 2.3 (a)) because for some alloys a significant ductility drop can occur in an intermediate temperature range below the solidus temperature (TS), often between 0.6 and 0.9TS. The two-phase mushy zone tends to shrink because of the solidification shrinkage and thermal contraction, but cannot shrink freely because its shrinkage is constrained by the much cooler bulk workpiece (Fig. 2.3 (a)). Thus, multi-axial tensile stresses are induced in the mushy zone that can separate growing dendritic grains from each other and cause cracking along the grain boundaries [98–102]. Cracks are often visible in the fusion zone, along grain boundaries, and the fracture surfaces show dendrites or cells [98–102].

Table 2.4 Formation of common defects in additive manufacturing of alloys.

<table>
<thead>
<tr>
<th>Defects</th>
<th>Alloys</th>
<th>Descriptions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solidification cracking</td>
<td>Al alloys, Ni alloys,</td>
<td>• Solidification cracking occurs when the tensile stress due to solidification shrinkage exceeds the yield strength and there is insufficient liquid metal to fill the crack.</td>
<td>[98–102]</td>
</tr>
<tr>
<td></td>
<td>austenitic stainless steels</td>
<td>• Solidification cracking is affected by tensile stress due to shrinkage, solidification temperature range, temperature-solid fraction relation, and solidification morphology.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Long columnar grains can result in solidification cracking.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Alloys with a high slope of temperature versus solid fraction plot are more susceptible to solidification cracking.</td>
<td></td>
</tr>
<tr>
<td>Liquation cracking</td>
<td>Al alloys, Ni alloys,</td>
<td>• Liquation cracking is caused by localized melting of low melting regions at a grain boundary under the influence of thermal strains. It is affected by the chemical compositions, the solidification range, solidification shrinkage, thermal contraction, and the presence of intermetallic compounds and precipitates.</td>
<td>[106–110]</td>
</tr>
<tr>
<td></td>
<td>austenitic stainless steels</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition changes due to selective vaporization</td>
<td>All alloys</td>
<td>• Alloying elements vaporize from the molten pool at different rates.</td>
<td>[113–117]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Selective vaporization of alloying elements results in composition change.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Composition change affects the microstructure, corrosion resistance, and mechanical properties of parts.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Vapor pressure of elements over the liquid alloy, local temperature, alloy composition, and pool surface area to volume ratio affect composition change.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Magnesium and zinc in aluminum alloys, chromium and manganese in steels, chromium in nickel alloys, and aluminum in titanium alloys are the most susceptible elements.</td>
<td></td>
</tr>
<tr>
<td>Lack of fusion</td>
<td>All alloys</td>
<td>• Insufficient fusional bonding between adjacent tracks or successive layers may result in the lack of fusion voids.</td>
<td>[119–123]</td>
</tr>
<tr>
<td>Porosity</td>
<td>All alloys</td>
<td>• Lack of fusion significantly degrades the tensile properties of parts.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Hydrogen, oxygen, and nitrogen in the atmosphere and shielding gas used during additive manufacturing can be entrapped inside the molten pool and result in gas porosities.</td>
<td>[125–136]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Gas entrapped inside powders made by gas atomization can also cause gas porosities.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• If vapors from the collapsed keyhole fail to escape the molten pool before it solidifies, keyhole porosities form.</td>
<td></td>
</tr>
</tbody>
</table>

Solidification cracking has been related to the nature of the temperature versus solid fraction curves. A simple index $|dT/d(f_S)^{1/2}|$ was used to evaluate the susceptibility to solidification cracking of different alloys, where $T$ is temperature and $f_S$ is the fraction of solid [103]. It was suggested that the maximum $|dT/d(f_S)^{1/2}|$ up to $(f_S)^{1/2} = 0.99$ (i.e., $f_S = 0.98$) is a convenient value for the index. This is because the maximum $|dT/d(f_S)^{1/2}|$ usually occurs near $(f_S)^{1/2} = 1$ and because beyond $f_S = 0.98$, the grains can bond to each other extensively to resist cracking. A steep variation in the temperature versus solid fraction plot means a very low liquid fraction near complete solidification over a relatively large temperature range. This depletion of the available liquid to heal the cracks over a large temperature range makes alloys susceptible to cracking. Fig. 2.3 (b) shows the variation of temperature with solid fraction for Al7075 and AlSi10Mg alloys [104]. It is observed that the change in temperature with the solid fraction is much steeper for Al7075 than AlSi10Mg, making Al7075 more susceptible to solidification cracking than AlSi10Mg.

This criterion for solidification cracking is useful to compare the susceptibilities of different alloys to solidification cracking. However, this criterion is devoid of any consideration of the specific additive manufacturing process or process variables. Comprehensive models for solidification cracking considering process variables are emerging [105].

2.3.2. Liquation cracking

Liquation cracking can occur during additive manufacturing of aluminum alloys, nickel-based alloys, and austenitic stainless steels [106–110]. It is caused by localized melting of low melting regions at grain boundaries under the influence of thermal strains. It generally occurs outside and adjacent to the fusion zone or in previously deposited layers where the temperature is below the solidus.
temperature of the alloy [106–110]. Liquation cracking depends on the alloy composition, the temperature range of solidification, solidification shrinkage, thermal contraction during cooling, and the presence of intermetallic compounds and precipitates [106–110].

Liquation cracking involves localized liquid formation (i.e., liquation) along grain boundaries as well as at isolated spots within grains. Liquation cracking can occur under significant tension induced by the solidifying/contracting mushy zone nearby. Alloys with a wide freezing temperature range are more susceptible. In arc welding, a suitably designed filler metal can be used to eliminate liquation cracking. A simple criterion was proposed by Kou and coworkers and verified experimentally [111]. It states that cracks occur if the fraction solid in the weld-metal is higher than that in the base-metal after the fraction solid reaches about 0.3. This criterion has been verified for Al and Mg alloys [111,112].

2.3.3. Composition change

Volatile alloying elements may selectively vaporize from the molten pool during additive manufacturing [113–117]. Different alloying elements vaporize at different rates at a given temperature. As a result, the chemical composition of the part can differ from that of the feedstock [113–117]. The rate of vaporization of an alloying element is affected by its vapor pressure above the liquid alloy,
which depends on the local temperature and the composition of the alloy. Loss of alloying elements and the composition change affect the microstructure, corrosion resistance, and mechanical properties of parts. Magnesium and zinc in aluminum alloys, chromium and manganese in steels, chromium in nickel alloys, and aluminum in titanium alloys are known to suffer from a significant change in composition (Fig. 2.3 (c)) during additive manufacturing [118].

The observed composition change [118] of alloying element $i$, $\Delta\%i$, can be related to its rate of evaporation through the following mass balance.

$$\Delta\%i = 100 \frac{J_i}{\lambda \rho v}$$  \hspace{1cm} (6)

where $J_i$ is the vaporization rate of an element $i$ per unit surface area, $A$ is the surface area, $\rho$ is the density of the weld metal, and $v$ is the volume of the alloy melted per unit time. The vaporization rate ($J_i$) is given by the Langmuir equation [118]:

$$J_i = \lambda \frac{P_i}{\sqrt{2 \pi M_i RT}}$$  \hspace{1cm} (7)

where $\lambda$ is a positive fraction that is related to the recondensation of the vaporized species that depends on the total pressure, $P_i$ is the equilibrium vapor pressure of $i$, $M_i$ is the molecular weight of $i$, $R$ is the gas constant, and $T$ is the temperature. The value of $\lambda$ is close to 1 at very low ambient pressures used typically when an electron beam is used as a heat source. When a laser beam is used and the ambient pressure is 1 atmosphere, a value of much lower than 1 is appropriate. The rate of evaporation per unit area depends on local temperature and varies spatially.

### 2.3.4. Lack of fusion voids

Lack of fusion voids [119–123] significantly degrade the tensile properties of parts and often lead to part rejection. Insufficient fusional bonding between adjacent tracks or successive layers may result in gaps between deposits known as the lack of fusion voids [119–123]. The undesirable space between adjacent tracks and successive layers is commonly attributed to insufficient feedstock melting as a result of incorrect process variable-alloy combinations. A heat source with low heat input, inappropriately fast scanning speed, thick layers, or high hatch spacing can result in such defects. Assuming that the lack of fusion is caused solely by a lack of overlap of fusion zones in adjacent tracks and layers, the geometric criteria (Fig. 2.3 (d)) for the lack of fusion have been proposed as follows [124]:

$$\left(\frac{H}{W}\right)^2 + \left(\frac{L}{D}\right)^2 \leq 1$$  \hspace{1cm} (8)

where $H$ is the hatch spacing, $W$ is melt-pool width, $L$ is layer thickness, and $D$ is melt-pool depth. The above equation indicates that if the width and the depth of the fusion zone are both 41.4% larger than the hatch spacing and layer thickness, respectively, the lack of fusion defects do not form.

### 2.3.5. Porosity

Hydrogen, oxygen, and nitrogen are frequently present in trace amounts in the environment, and they are soluble in the alloys to varying degrees. Molten aluminum alloys, for example, absorb varying amounts of all of these gases from the atmosphere. Hydrogen is more soluble in liquid aluminum and magnesium than in solid phases. Hydrogen and nitrogen also dissolve in steels and can be trapped as porosity in solid alloys. In addition, shielding gas can be entrapped inside the molten pool and result in gas porosity [125–129]. Gas entrapped inside powders made by gas atomization can also cause gas porosity [125–129]. During the additive manufacturing processes, ambient gases may also dissolve in the part. For example, hydrogen, nitrogen, and oxygen, present at low concentrations in the environment may dissolve [130] in the fusion zone:

$$\frac{1}{2} G_2 = \mathcal{G}$$  \hspace{1cm} (9)

$$a_0 = \mathcal{K}_0 (p_{G_2})^{1/2}$$  \hspace{1cm} (10)

where $G_2$ is a diatomic gas such as hydrogen, nitrogen, and oxygen, $p_{G_2}$ is the partial pressure of the gas, $a_0$ is the activity of the dissolved species in the alloy. The local concentration of dissolved gas can be found from the activity versus composition relation. When the ambient environment contains a plasma consisting of diatomic gases, dissociated monatomic species in their ionic, excited, and ground states, and electrons, the extent of dissolution of the gases [131] is significantly higher than that predicted by equation (10). The theory and the calculation procedure are available in the literature on fusion welding [131].

If the gas bubbles can escape from the molten pool before its solidification, gas porosities do not form. The escape of the bubbles depends on the size of the fusion zone, the thermophysical properties of the alloy, and process parameters. Bubbles can move within the fusion zone at the prevailing velocity of the liquid metal. Furthermore, the buoyancy force causes the bubbles to rise. The rising velocity ($u$) of spherical bubbles can be estimated roughly using the Stokes law, which is valid for low Reynolds numbers ($<2$) and is given by:

$$u = 2r^2 \Delta \rho g / (9 \mu)$$  \hspace{1cm} (11)

where $r$ is the radius of the bubble, $\Delta \rho$ is the density difference between the liquid and the gas bubble, $g$ is the acceleration due to gravity, and $\mu$ is the viscosity of the liquid. The size of the bubble, as well as the time available for bubble growth and escape, are important factors in the formation of porosity. Low liquid viscosity and large bubble radius increase the likelihood of bubbles escaping.
from the fusion zone. Rapid cooling, on the other hand, gives bubbles less time to escape.

Alloys can vaporize during additive manufacturing with a high-power density laser or electron beam. The recoil pressure produced by the vapors displaces the liquid metal and forms a vapor cavity, called a keyhole [132–136]. Keyholes are often unstable and the lower portion of the keyhole may collapse [134]. A portion of the vapors from the collapsed keyhole is trapped within the liquid pool. If the vapor packet fails to escape the molten pool before it solidifies, keyhole porosities form [132–136].

3. Control of grain structure, phases, and defects in steels

Printed parts of austenitic stainless steels, martensitic steels, duplex stainless steels, and other steels often exhibit long columnar grains that result in poor tensile properties. In addition, they form various phases that affect the mechanical properties. Cracking, lack of fusion, porosity, and composition change due to selective vaporization of the alloying elements are also common in printed steel parts. Table 3.1 provides a selected examples of controlling grain structure, phases, and defects in additively manufactured steel parts. The control strategies for each type of steels are reviewed in this section.

3.1. Austenitic stainless steels

Austenitic stainless steels contain high concentrations of chromium (\(>17\) wt%) and appreciable amounts of nickel (typically 8%) and/or manganese to stabilize austenite. They are widely used in chemical, nuclear, and oil and gas industries for their excellent

<table>
<thead>
<tr>
<th>Objective</th>
<th>Alloy</th>
<th>AM process</th>
<th>Description of control strategy</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control of grain structure</td>
<td>SS 316</td>
<td>PBF-L</td>
<td>Grain orientation was changed from the usual (〈001〉) to (〈110〉) using small hatch spacings and high laser power</td>
<td>[155]</td>
</tr>
<tr>
<td></td>
<td>H13 tool steel</td>
<td>PBF-L</td>
<td>Low heat input attained by reducing the heat source power and rapid scanning increased the cooling rates and decreased the grain size and dendritic arm spacing</td>
<td>[171,177]</td>
</tr>
<tr>
<td></td>
<td>CrNiMo low alloy steel</td>
<td>PBF-L</td>
<td>Grain size of the cellular solidification structure was reduced using faster scanning</td>
<td>[192]</td>
</tr>
<tr>
<td></td>
<td>Reduced activation</td>
<td>PBF-L</td>
<td>austenite formation was controlled by adjusting the local temperature gradient by implementing different scanning strategies</td>
<td>[193]</td>
</tr>
<tr>
<td></td>
<td>ferritic-martensitic steel</td>
<td>PBF-L</td>
<td>Silicon particles were added as grain refiners to refine the grains</td>
<td>[188]</td>
</tr>
<tr>
<td></td>
<td>High-strength low alloy steel</td>
<td>PBF-L</td>
<td>High melting point tellurium nanoparticles were used to refine the grains since they promoted heterogeneous nucleation</td>
<td>[252]</td>
</tr>
<tr>
<td></td>
<td>18-Ni 300 Maraging steel</td>
<td>PBF-L</td>
<td>Coarsening of grains was observed at higher heat treatment times and temperatures</td>
<td>[204]</td>
</tr>
<tr>
<td></td>
<td>15-5PH stainless steel</td>
<td>PBF-L</td>
<td>Different scanning strategies were used to control the temperature gradient and cooling rates to refine grains</td>
<td>[218]</td>
</tr>
<tr>
<td></td>
<td>Duplex DSS 2507</td>
<td>PBF-L</td>
<td>Rapid scanning reduced the grain size</td>
<td>[229]</td>
</tr>
<tr>
<td></td>
<td>22Cr duplex steel</td>
<td>PBF-L</td>
<td>Low heat input resulted in high cooling rates and small grains</td>
<td>[221]</td>
</tr>
<tr>
<td></td>
<td>ODS steel</td>
<td>PBF-L</td>
<td>An addition of 5 wt% yttria significantly refined the grain</td>
<td>[251]</td>
</tr>
<tr>
<td></td>
<td>ODS steel</td>
<td>PBF-L</td>
<td>High melting point tellurium nanoparticles were used to refine the grains since they promoted heterogeneous nucleation</td>
<td>[252]</td>
</tr>
<tr>
<td>Control of phases</td>
<td>SS 316</td>
<td>DED-L</td>
<td>The microsegregation in the intercellular regions resulted in the enrichment of chromium and molybdenum both of which stabilized ferrite</td>
<td>[139,143]</td>
</tr>
<tr>
<td></td>
<td>SS 316</td>
<td>PBF-L</td>
<td>High cooling rates resulted in a very fine microstructure that was claimed to hinder martensite formation</td>
<td>[147]</td>
</tr>
<tr>
<td></td>
<td>H13 tool steel</td>
<td>DED-L</td>
<td>Post-process heat treatment was used to temper the martensite and improve the toughness</td>
<td>[178]</td>
</tr>
<tr>
<td></td>
<td>18-Ni 300 Maraging steel</td>
<td>PBF-L</td>
<td>The size, amount, and distribution of the intermetallic compounds were controlled by adjusting the heat treatment temperatures and times</td>
<td>[199,202]</td>
</tr>
<tr>
<td></td>
<td>15-5PH stainless steel</td>
<td>PBF-L</td>
<td>The size, amount, and distribution of the intermetallic compounds were controlled by adjusting the heat treatment temperatures and times</td>
<td>[199,202]</td>
</tr>
<tr>
<td></td>
<td>Duplex stainless steel</td>
<td>DED-L</td>
<td>Post-process heat treatment was used in adjusting the shape, size, and quantity of the precipitates</td>
<td>[219]</td>
</tr>
<tr>
<td></td>
<td>Fe-14Cr stainless steel</td>
<td>DED-L</td>
<td>Amount of dispersed oxides were controlled by adjusting the heat input, adding oxide-forming elements, and changing the chemical composition</td>
<td>[250]</td>
</tr>
<tr>
<td>Control of defects</td>
<td>H13 tool steel</td>
<td>PBF-L</td>
<td>Solidification cracking was minimized by adjusting the laser power, scanning speed, layer thickness, and hatch spacing</td>
<td>[174]</td>
</tr>
<tr>
<td></td>
<td>Duplex stainless steel</td>
<td>PBF-L</td>
<td>The lack of fusion defects were mitigated using higher power</td>
<td>[223]</td>
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<tr>
<td></td>
<td>TRIP steel</td>
<td>PBF-L</td>
<td>The lack of fusion was controlled by increasing the heat input at a higher laser power</td>
<td>[272]</td>
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<tr>
<td></td>
<td>H13 tool steel</td>
<td>PBF-L</td>
<td>The lack of fusion defects were minimized by increasing the energy density of the laser beam</td>
<td>[174]</td>
</tr>
<tr>
<td></td>
<td>Maraging steel</td>
<td>PBF-L</td>
<td>Scanning with a shorter track length reduced the lack of fusion</td>
<td>[210]</td>
</tr>
<tr>
<td></td>
<td>2205 duplex steel</td>
<td>DED-L</td>
<td>Gas porosity was reduced at high interlayer temperature</td>
<td>[233]</td>
</tr>
<tr>
<td></td>
<td>CrNiMo low alloy steel</td>
<td>PBF-L</td>
<td>The higher energy density of the laser beam reduced gas porosity</td>
<td>[187]</td>
</tr>
<tr>
<td></td>
<td>H13 tool steel</td>
<td>DED-L</td>
<td>Mn loss decreased with a reduction in laser energy input</td>
<td>[176]</td>
</tr>
</tbody>
</table>
corrosion and oxidation resistance, fabricability, and good mechanical properties. Their high thermal expansion coefficient precludes their use in some power plants and other applications.

### 3.1.1. Microstructure control

Additively manufactured austenitic stainless steels such as 316 L and 304 contain mainly austenite [137] with or without a small amount of retained δ ferrite [138,139] and/or martensite [140]. For the solidification of austenitic stainless steels, the solidification mode depends on the nickel and chromium equivalents of the alloys and solidifies primarily in either ferrite–austenite or austenite mode [141,142]. Typical microstructures of austenitic stainless steels in powder bed fusion and directed energy deposition are somewhat different from each other. In the directed energy deposition of 316L stainless steel, the microsegregation in the intercellular regions results in the enrichment of chromium and molybdenum both of which stabilize ferrite, and between 8 and 10% ferrite has been observed in the microstructure [139,143]. Segregation of ferrite stabilizers also occurs in powder bed fusion. However, the cooling rates are high in the powder bed fusion process and the extent of segregation is insufficient to stabilize ferrite [144,145], and ferrite is not commonly observed in the microstructure. Typical microstructures of austenitic stainless steel components made by additive manufacturing are compared with the microstructural features of other steels in Fig. 3.1.1. Because of the high cooling rates encountered in powder bed fusion, the microstructures are typically quite fine [146]. PBF-L produced 316L has a very fine microstructure that is claimed to hinder martensite formation [147]. SS 316L components produced by powder bed fusion show high elongation at fracture because of twinning-induced plasticity [148]. The typical microstructure exhibits several important features in different length scales. The solidification microstructure can be columnar or equiaxed or a mixture of both at the submillimeter scale.

![Microstructural features of different steels](image)

**Fig. 3.1.1.** Typical microstructures [137] of the different steels produced conventionally and after additive manufacturing. Depending on processing conditions, different microstructures may be observed after AM. ppt.: precipitates, ret.: retained, α: ferrite, bcc, α’: martensite bcc/bct, γ: austenite, fcc.
The subgrain features include numerous very fine cells, of dimensions typically smaller than a micrometer \[145\] and cell boundaries of the order of about 100 nm with the boundaries lined with networks of dislocations. The size of the oxide inclusions is typically 50 nm but can vary significantly in the range between 5 nm to micrometers and chemical composition vary from spinels to many other complex compositions depending on the alloy composition and processing conditions. Fig. 3.1.2 shows important features of additively manufactured 316L stainless steel at different length scales \[145\].

Although the microstructures of these additively manufactured steels are dominated by austenite, it is the hierarchical microstructure \[145,146\] that has attracted much attention because the microstructure is thought to be the underlying source of the unique combination of outstanding properties not achieved in conventionally made parts. In most alloys, the improvements in the strength of an alloy resulting from heat treatment are accompanied by a decrease in ductility. The additive manufacturing of austenitic stainless steel is an exception because a higher strength is achieved without sacrificing ductility \[145\]. These favorable properties can further be improved through metallurgical post-processing of DED-wire 304L SS for increased ductility and reduced AM texture \[149,150\]. Optimizing the features of the hierarchical microstructure is an important goal to achieve superior properties in austenitic stainless steels.

Wang et al. suggested that the microstructural features can be controlled by adjusting process parameters \[145\]. Control of cooling rates and temperature gradients is possible by adjusting power, scanning speed, and scanning pattern. Although simultaneous improvements in both strength and ductility not achievable in conventional processing is an exciting possibility, more work is needed to correlate process variables with the many features of the hierarchical microstructure excluding the parameter space where common defects compromise properties.

### 3.1.2. Grain structure control

Elongated columnar grains \[151,152\] in the building direction are common in the powder bed fusion of austenitic stainless steels such as SS304. High volumetric energy density was found to be responsible for strong texture in \([100]\) direction in parts made with SS316 austenitic stainless steel \[153\]. However, at lower volumetric energy densities, a multicomponent texture was obtained which was attributed to the high nucleation rate and the deviation of grain orientation from the \([100]\) easy growth direction \[153\]. Some austenitic stainless steels such as 304L often form annealing twins during additive manufacturing because of their low stacking fault energy \[153\].

During solidification of cubic materials, the dendrites grow along the dominant heat flow direction perpendicular to the local fusion zone curvature along the \([001]\) direction which is the fastest growth direction. As a result, a crystallographic texture with the \([001]\) direction along the build direction is commonly observed \[154\]. The heat flow direction varies locally depending on the shape of the fusion zone although most heat is extracted to the base plate for small components. Since the shape of the fusion zone can be controlled by adjusting process parameters, particularly scan parameters and alloy composition including the concentrations of the surface-active elements, the texture can be controlled. It has been shown \[155\] that the crystallographic texture can be changed from the usual \([001]\) to \([110]\) using small hatch spacings and high laser power. It has also been shown that texture can be controlled by scanning strategy in cubic alloys \[156\]. Scanning strategy can also avoid anisotropy of most mechanical properties. Grain size and topology also depend on the process variables and alloy properties and affect both strength and ductility. Although control of grain structure and topology can be implemented by controlling process parameters, care must be taken to avoid defects that are common in additively manufactured parts.

![Fig. 3.1.2. Microstructural features of a 316L austenitic stainless steel part at various length scales. a) Various length scales of the microstructural features. b) EBSD inverse pole figure mapping showing the grain orientations. C) SEM image of the cross-section showing high-angle grain boundaries, fusion boundaries, and the cellular solidification structure. d) Bright-field TEM image of the cellular structure showing dislocation networks in the cell boundaries. e) high-angle annular dark-field scanning TEM image of the solidification cells showing oxide particles \[145\]. The figure is adapted from reference \[137\].](image-url)
3.1.3. Control of defects

Common defects in parts made using austenitic stainless steel parts include porosity and lack of fusion, residual stress and distortion, and anisotropy [2]. Pores in the components often originate from dissolved oxygen and nitrogen in the powder and wire feedstocks [153]. These pores are typically round in shape and small, of the order of a few tens of micrometers in diameter and can be controlled by the way the feedstocks are made. Also, some alloys are more susceptible to gas porosity because of their high solubility of common impurities such as oxygen, nitrogen, and hydrogen in the feedstock. Larger voids typically deviate from the spherical shape and may appear from a lack of fusion [118,157] or instability of a keyhole [158]. They affect fatigue property [159,160], corrosion resistance [161,162], and other mechanical properties such as wear resistance [163,164]. Residual stresses arise in additively manufactured parts because of substantial temperature gradients and repeated heating and cooling that varies with location within the part. Both process variables and alloy properties affect residual stresses and distortion. While preventing these defects during the manufacturing of parts is desirable, often post-processing is a practical way to alleviate these defects. Hot isostatic pressing is effective in removing small gas porosities to a large extent.

Appropriate standards for the feedstock, particularly the powder manufacturing method, and limits on concentrations of oxygen, nitrogen, and hydrogen would be beneficial in preventing small gas-induced pores in parts. Lack of fusion defects are prevented by large fusion zone sizes, smaller hatch spacing, and thinner layer thickness, all of which promote sufficient overlap of the fusion zone between different tracks in a layer and between different layers [157]. However, the build time increases when tracks are closely spaced and when thinner layers are used. So, increasing heat source power and reducing scanning speed can also increase the overlap of the fusion zone between adjacent tracks and layers and increase part density. If large pores are found to originate from the keyhole instability, process variables have to be adjusted to enhance the stability of the keyhole. Vigorous recirculation of large melt pools owing to Marangoni convection has been suggested as a mechanism for the removal of porosities in austenitic steel processed using high volumetric energy density [153]. Although there is no definitive protocol for reducing keyhole instability in austenitic stainless steels, previous work in other alloy systems indicates that increasing power density may result in increased stability of the keyhole and reduce keyhole-induced porosity [158]. It was found that the density of the additively manufactured parts was higher when a higher volumetric energy density was used [153]. Previous works on the mitigation of residual stresses and strains in additive manufacturing show significant benefits from preheating. A scanning strategy is also used to reduce residual stresses and distortion as well as to control grain structure [3]. In addition, heat treatment after the component is made is also used to reduce residual stresses and distortion and reduce property anisotropy [3]. Although post-processing is widely used to improve the microstructure and properties of additively manufactured austenitic stainless steel components, optimization of heat treatment parameters is still undertaken by trial and error guided by the previous work on the heat treatment of the conventionally manufactured cast and wrought materials.

3.2. Martensitic steels

This section reviews two categories of martensitic steels (1) steels that utilize the martensitic transformation as the dominant strengthening mechanism and (2) steels that develop low carbon, soft martensite structure but are mainly strengthened via subsequent aging reactions by forming intermetallic precipitates [165]. The first category includes tool steels, low alloy steels, and ferritic-martensitic steels, while those in the second group are maraging steels and precipitation hardening (PH) steels [165]. These steels are introduced below.

- Tool steels [56,166–186] are high carbon steels containing carbide-forming elements such as Cr, V, Mo, Nb, and W. These steels are used to make tools such as drills, punches, dies, and other cutting tools. These steels generally exhibit a hard martensite matrix with dispersed carbides that provide excellent wear resistance and hardness. Although several tool steels are used, H13 tool steel is the most common in additive manufacturing. We have focused on H13 tool steel in this review.

- Low alloy steels [42,187–191] typically contain Ni, Cr, and Mo and carbon content between 0.3 and 0.4 wt%. Commonly used low alloy steels are 4140, 4340, and HSLA 100. They are used for machine parts, connecting rods, and crankshafts. Rapid cooling during AM forms martensite and carbides of Ni, Cr, and Mo that provide high hardness.

- Steels with ferritic-martensitic [44,192–197] crystal structures have low thermal expansion coefficients, high thermal conductivity, and high resistance to void swelling which make these steels popular in both fossil fuel and nuclear power industries. These steels contain from 2% to 12% Cr and are tempered to transform the martensite into tempered martensite and ferrite. Grade 91 (9% Cr) and HT-9 (12% Cr) are the most common ferritic-martensite steels for AM.

- Maraging steels [198–213] are strengthened by the precipitation of one or more nano-scale intermetallic compounds in a soft Fe-Ni martensite matrix. These steels have excellent toughness where the soft martensite matrix provides the ductility and the high strength originates because of the presence of the intermetallic compounds. In addition, they have good weldability and printability without hydrogen-induced cracking issues. These properties make maraging steels suitable for airframe structural applications (landing gear) and various dies and molds for metal forming. The 18 Ni-300 maraging steel is the most commonly used and discussed in this review.

- Precipitation hardened (PH) steels [214–220] form a soft martensitic structure that allows components to be easily formed or machined and provides good ductility. Their strength is developed via precipitation hardening of fine intermetallic phases during aging treatments after deposition. The 17–4 PH, 15–5 PH, and 13–8 PH are the most commonly used PH stainless steel.

For these martensitic steels, the mechanical properties are largely contributed by the formation of martensitic phases and secondary phases such as intermetallic compounds. Therefore, most of the research has been performed to control these phases by adjusting the
processing conditions and performing post-process heat treatment at different aging times and temperatures. A relatively lower volume of literature is available on controlling grain structures of these steels by adjusting process variables such as heat input. Primarily, these steels are susceptible to lack of fusion, porosity, and cracking and several attempts have been made to control these defects. This section reviews the common strategies to control grain structure, phases, and defects in martensitic steels.

3.2.1. Control of grain structure

Martensitic steels primarily exhibit cellular or dendritic grain structure. The size of cellular grains and the arm spacings of dendrites are controlled by adjusting the processing conditions. Laser power, scanning speed, preheating temperature, layer thickness, and hatch spacing are adjusted to alter the temperature gradient, solidification growth rates, and cooling rates to control the solidification morphologies and grain structure. For H13 tool steels, the grain structure consists of a cellular solidification microstructure with intercellular carbides or dendritic morphology [175]. The size of grains with cellular morphology and the arm spacing of dendritic structures can be controlled by adjusting the process variables [171,176,177]. For example, low heat input attained by reducing the heat source power and rapid scanning increases the cooling rates and decreases the grain size and dendritic arm spacing [171,176,177]. The grain size of the cellular solidification structure during PBF-L of H13 tool steel can be significantly reduced by printing the parts using faster scanning speeds [171]. Finer grains improve the mechanical properties of parts. A similar approach was also used to control grain structure for other alloys such as PBF-L of CrNiMo low alloy steel and PBF-L of a reduced activation ferritic-martensitic steel [192]. Fig. 3.2.1 shows the grain structures [192] determined using EBSD for a reduced activation ferritic-martensitic steel component made using two energy densities of the laser beam during PBF-L. Components were produced using a zig-zag scanning pattern and a 90° rotation of the scan direction between layers [192]. The sample produced with a lower energy density displayed a “checkerboard” pattern when viewed from above (Fig. 3.2.1 (a)) and stacked rows of melt pool regions of high-aspect-ratio in the front view (Fig. 3.2.1 (b)). In contrast, the sample produced using high energy density was characterized by a more random and equiaxed microstructure in the top view (Fig. 3.2.1 (c)) with a stack of melt pools of lower aspect ratios (Fig. 3.2.1 (d)). Both samples revealed a microstructure consisting of two different grain sizes [192]. The same group of authors also showed that grain structure during PBF-L of a reduced activation ferritic-martensitic steel can be controlled by adjusting the local temperature gradient by implementing different scanning strategies [193].

Apart from the adjustment of processing conditions to refine grains, a few attempts have been made to add inoculants to refine grains during AM of martensitic steels. For example, SiC particles were added during DED-GMA of high-strength low alloy steel to refine the grains [188]. However, the size and amount of the particles were determined by trials. A comprehensive theoretical and experimental investigation is needed to make this method commercially viable.

During the solidification of maraging steels, the primary solid γ phase forms at the interface between the solid and liquid phases along the preferential 〈001〉 solidification direction [210]. During further cooling, at temperatures lower than the martensite start temperature (approximately 200 °C), α phase martensite starts forming within the prior γ phase grain boundaries. The prior γ phase grain morphology [204,207] is either cellular (Fig. 3.2.2 (a)) or a mixture of cellular and dendritic structures (Fig. 3.2.2 (b)). For maraging steels, the mechanical properties are largely affected by the martensite and precipitates of intermetallic compounds formed during aging. Therefore, more research has been done to control the phases (see Section 3.2.2) compared to that for controlling the

![Fig. 3.2.1. Grain structures characterized by EBSD for a reduced activation ferritic-martensitic steel made by PBF-L [192]. Grain structures are shown at (a) top and (b) front views for the sample made using 98 J/mm³ energy density and at (c) top and (d) front views for the sample made using 209 J/mm³ energy density.](image-url)
grain structure. A few examples of controlling grain structure in maraging steels include the application of post-process heat treatment [204]. In this study, different combinations of heat treatment temperatures and times were used to control the size of the cellular grains. Coarsening of grains was observed at higher heat treatment times and temperatures [204]. High flow rates of the shielding gas during additive manufacturing of maraging steel resulted in rapid cooling and refined grains [209].

Similar to the maraging steels, post-process heat treatment is also used to control the grain structure of additively manufactured PH steels. For example, Fig. 3.2.3 shows that the post-process heat treatment of 15–5PH stainless steel parts fabricated by DED-L [217] homogenized the grain structure and improved the mechanical properties. Grain structure during PBF-L of 15–5PH stainless steel parts can be controlled by adjusting the local temperature gradient by implementing different scanning strategies [218]. In this study, four different scanning strategies were used (Fig. 3.2.4). The island scanning strategy with the small hatch length was the most effective in refining the grains. However, more work is needed to find a quantitative basis for selecting an appropriate scanning strategy and processing conditions to achieve the desired grain structure.

![Fig. 3.2.2. SEM images showing the (a) cellular [207] and (b) cellular and dendritic [204] microstructure in 18Ni-300 maraging steel parts made by PBF-L.](image1)

![Fig. 3.2.3. EBSD orientation maps showing grains structures of 15–5PH stainless steel parts fabricated by DED-L [217]. Grain structures are shown for the as-fabricated part on (a) horizontal plane and (b) transverse plane and for the heat-treated part on (a) horizontal plane and (b) transverse plane.](image2)
3.2.2 Control of phases

Tool steels, low alloy steels, and ferritic-martensitic steels form hard martensite due to the rapid cooling rates during AM. The martensite increases the strength and hardness but significantly reduces the ductility and toughness. Post-process heat treatment is often employed to temper the martensite and improve the toughness [173,178]. For example, Fig. 3.2.5 shows the change in the microstructure of the H13 part made by PBF-L at different heat treatment temperatures [173]. When the temperature is between 350

![Fig. 3.2.4. EBSD orientation maps showing grains structures of 15–5PH stainless steel parts fabricated by PBF-L [218] with (a) unidirectional, (b) bidirectional, (c) cross-directional, and (d) island scanning strategies.](image1)

![Fig. 3.2.5. Microstructure of H13 tool steel parts produced by DED-L and heat-treated at different temperatures: (a) 350C, (b) 450C, (c) 550C, (d) 600C, and (e) 650C. Figure courtesy: Professor Min Zhang from Soochow University, China.](image2)
and 450 °C, there was no big difference between the heat-treated samples. Only a small fraction of martensite was transformed into tempered martensite and formed Cr and V-rich carbides. However, when the tempering temperature increased, more carbon precipitated and reacted with Cr and V forming alloy carbides (Mo2C, VC, Cr7C3, and Cr23C6). These carbides significantly improve toughness [173]. Post-process heat treatment is used to temper martensite and improve the toughness of martensitic steels. However, post-process heat treatment adds an extra cost and is thus often not desirable.

Tempering of martensite also occurs because of multiple heating and cooling cycles during the deposition of many layers and hatches during AM. This process is often called in-situ heat treatment. The martensite formed in a deposited layer may be transformed partially or fully to tempered martensite during the deposition of subsequent layers. This phenomenon has been reported for DED-L of H13 tool steels [179–182], DED-GMA of a high strength low alloy steel [42], and DED-L of grade 91 steel [194]. It is evident that the extent of transformation of martensite into tempered martensite is affected by the local thermal cycles [179,180] and thus can be controlled by adjusting the heat input, layer thickness, and scanning strategies.

For maraging and precipitation-hardened steels the mechanical properties of the parts are affected by the size, amount, and distributions of the secondary phases such as micro and nanoscale intermetallic compounds. As-deposited maraging steel contains a soft, heavily dislocated iron-nickel lath (untwinned) martensite. Subsequent aging produces a fine dispersion of intermetallic phases (Fig. 3.2.6) along dislocations left by the martensitic transformation [201,205]. Additional alloying agents include Mo, which forms a Ni3Mo intermetallic phase, and Al and Ti, which are incorporated into a Ni3(Ti, Al) intermetallic precipitate (Fig. 3.2.6). Co does not form precipitates but raises the martensite start temperature and promotes the formation of Ni3Mo by lowering the solubility of Mo in the matrix [201,205]. Fig. 3.2.7 (a) and (b) show that the Ti and Ni enriched precipitates are spherical but both spherical and irregular shapes are observed for Mo enriched precipitates [202]. The size, amount, and distribution of the intermetallic compounds are controlled by adjusting the heat treatment temperatures and times [199,202,208,211]. For example, an increase in the heat treatment temperature supports the precipitation process and increases the size of the precipitates (Fig. 3.2.7 (c)) which significantly affects the mechanical properties of the part.

Fig. 3.2.6. A high-magnification EBSD and corresponding EDS element maps of various elements for an 18Ni-300 maraging steel part made by DED-L. The phase map in figure (a) indicates the location of the retained austenite in the interdendritic areas. Figure (b) shows the enrichment of Ti, Mo, and Ni in these regions of retained austenite. Co does not generally form intermetallic compounds but alters the martensitic start temperature [205].
Controlling the time and temperature of the post-process heat treatment was also helpful in adjusting the shape, size, and quantity of the precipitates and thus achieving the desired properties of 15–5 PH steel parts made by powder bed fusion [219]. However, care should be taken in selecting the range of heat treatment temperatures and times because excessive heat treatment is known to cause the decomposition of the martensite and reversion to austenite for maraging steels [206].

Fig. 3.2.7. Size of (a) spherical Ti and Ni enriched precipitates and (b) spherical and irregular-shaped Mo enriched precipitates. (c) An increase in the average size of the precipitates with the aging time at 510 °C aging temperature. All figures are for 18Ni-300 maraging steel parts made by PBF-L [202].

Fig. 3.2.8. Defects in H13 tool steel parts made by PBF-L (a) lack of fusion between melt pools, (b) gas pores within melt pool, and (c) crack along deposition planes [174]. Process maps show how to control (d) cracking and (e) porosity by adjusting the process parameters [174].
Recently, it has been reported [212,213] that the addition of just 0.39 wt% of copper can significantly refine the martensitic lath size during DED-GMA of maraging steels and affect the mechanical properties. However, the detailed mechanism of refining the martensitic lath is not known and needs further research.

3.2.3. Control of defects

Martensitic steels are susceptible to composition change, lack of fusion, porosity, and cracking. Composition change occurs due to the loss of alloying elements due to their selective vaporization during AM. For example, Mn loss [176] was observed during DED-L of H13 tool steel which was shown to decrease with a reduction in laser energy input. Solidification cracking or hot tearing is possible during AM of martensitic steels. Hydrogen-induced cracking of martensitic steels, similar to that encountered in welding processes using flux coatings contaminated by moisture and exacerated by residual tensile stress, is possible for AM of martensitic steels owing to the presence of hard “susceptible” microstructures and residual stress. Reheat cracking, involving precipitation of carbides in grain interiors causing wedge cracking due to grain boundary sliding is also found during AM of martensitic steels. Cracking is observed in PBF-L of H13 tool steel [174], PBF-L of high-speed tool steels [184], and PBF-L of maraging steels [202]. For example, Fig. 3.2.8 shows various types of defects in PBF-L of H13 tool steel where Fig. 3.2.8 (c) shows long cracks in the printed part [174]. Such cracks were shown to be minimized [174] by adjusting the laser power, scanning speed, layer thickness, and hatch spacing (Fig. 3.2.8 (d)). Voids generated due to the lack of fusion and gas porosities degrade the mechanical properties of parts. Such defects are observed in PBF-L of H13 tool steel [174,183], maraging steels [199,200,202], 15-5PH steel [218], and 17-4PH steel [220]. For example, Fig. 3.2.8 (a) and (b) show the lack of fusion voids and gas pores, respectively, in H13 tool steel parts made by PBF-L [174]. Such voids were minimized by increasing the energy density of the laser beam (Fig. 3.2.8 (e)). The higher energy density of the laser beam also reduced porosity during PBF-L of CrNiMo low alloy steel [187]. Several attempts have also been made to minimize these defects by adjusting the process variables [200,206,209,210] for AM of maraging steels. For example, the lack of fusion voids was minimized [200] by increasing the energy density during PBF-L of 18Ni-300 maraging steel which significantly improved the density of the part (Fig. 3.2.9). The number of voids was also reduced by adjusting the scanning pattern [210]. Scanning with a shorter track length resulted in the return of the heat source to its initial position quickly, thus enhancing heat accumulation, a larger pool, and reduced lack of fusion voids.

3.3. Duplex stainless steels

Duplex stainless steels have higher concentrations of chromium (>19.5 wt%) and typically lower concentrations of nickel (3 to 8.5%) than those in austenitic stainless steels. A high concentration of chromium stabilizes the primary $\delta$-ferrite that forms during solidification and austenite forms subsequently from ferrite during cooling. Nearly equal amounts of $\delta$-ferrite and austenite in the microstructure of duplex stainless steels provide excellent combinations of strength and ductility. The tendency to form austenite in duplex steels is influenced by the ratio of the chromium equivalent, $C_{eq}$, and nickel equivalent, $Ni_{eq}$. $C_{eq}$ depends on the concentration of the ferrite stabilizing elements such as Cr and Mo, and $Ni_{eq}$ is computed from the concentrations of austenite stabilizing elements such as Ni and N. A low value of $C_{eq}/Ni_{eq}$ facilitates the formation of austenite [18].

In addition to the formation of ferrite and austenite, the alloying elements also contribute to solid solution strengthening. A high concentration of nitrogen in these steels increases the tendency to both form austenite and nitride precipitates. Properties of the duplex steel parts also depend on the amount and size distribution of carbide precipitates, $M_2C_3$ and $M_23C_6$ where M is Fe or Cr. The microstructure also contains brittle intermetallic phases of Fe and Cr, such as the sigma phase ($\sigma$) which is rich in iron, chromium, and molybdenum and has a tetragonal crystal structure. Duplex steels are relatively more affordable than austenitic stainless steels because of their lower nickel concentrations and they provide excellent resistance to pitting and crevice corrosion at relatively low-temperature applications in oil and gas, shipbuilding, petrochemical, and other industries.
3.3.1. Microstructure control

During the additive manufacturing processes, the time–temperature history affects the kinetics of the transformation of δ-ferrite to austenite and therefore the proportion of the ferrite and austenite, and the resulting properties of the part. The optimum amount of austenite, about 50% in the final microstructure, requires slow cooling to provide enough time for the solid-state transformation of ferrite to austenite. During additive manufacturing, particularly powder bed fusion, the cooling rate in the 1200 to 800 °C range is too rapid to transform ferrite to the optimum amount of austenite. For example, Jiang et al. [221] studied the PBF-L of two duplex steels 22.5Cr-5.5Ni-3.5Mo-0.21 N and 25.7Cr-7.3Ni-4.4Mo-0.3 N and found nearly 100% ferrite in the microstructure. In the powder bed fusion process, the time for the transformation of δ-ferrite to austenite is insufficient to achieve 50% austenite, and the microstructure of the as-built part is composed mainly of ferrite. Fig. 3.3.1 shows the ferrite microstructure of PBF-L 2507 duplex stainless steel [222] and the EBSD shows the single-phase ferritic structure with a mosaic-type macrostructure [222]. If the steel contains significant amounts of nitrogen, nitride inclusions are also observed at the grain boundaries [223]. Post-built heat treatment is necessary at temperatures above 900 °C to achieve the necessary amount of austenite. Care must be taken to select the temperature and duration of the heat treatment to prevent significant amounts of brittle phases such as the sigma phase while forming the necessary amount of austenite. For example, Lams et al. [224] increased austenite percentage from 38.5% to 57.6% by hot isostatic pressing at 1170 °C and 145 MPa for 3 h after the DED of duplex 2205.

In the DED-GMA process, the heat input per unit length is higher than that of laser and electron beam based PBF and DED processes. As a result, the cooling rates of the DED-GMA process are lower than those in the PBF and DED processes. So in DED-GMA, δ-ferrite has more time to transform to austenite and higher austenite content is observed in the microstructure. Also, the brittle intermetallic phases such as the sigma phase can form during the slow cooling and the microstructure can contain coarse grains. Control of heat input is useful for achieving the desired grain structure [18] and to increase the ferrite concentration in additively manufactured duplex steel parts [225]. Eriksson et al. [226] found that the ferrite content in wire-arc duplex steel 2760 ranged between 15% and 27%, depending on the heat input. The ferrite content tended to decrease with increasing arc energy [227]. At high heat inputs, there is more time for the ferrite to transform to Widmanstatten type austenite at ferrite grain boundaries at elevated temperatures and as a result, the austenite fraction in the microstructure is high at high heat inputs. The σ phase can be prevented in the as-produced state [227] by controlling heat input. For the 2507 alloy, the predominantly ferritic microstructure in the as-produced state has good yield strength [228] and UTS of PBF-L produced part. The fracture occurs in a ductile mode and the elongation at fracture is 8%. Heat treatment at elevated temperatures such as 1200 °C leads to some σ phase precipitates [228] which makes the parts quite brittle at room temperature with only 1.8% elongation at fracture and relatively low strength which is attributed to the presence of austenite. It is possible to reach 55% austenite and 45% ferrite and > 99.5% relative density with heat treatment of the parts [137].

Where possible, adjustment of heat input may affect the proportion of ferrite and austenite in the microstructure. However, duplex steel parts produced by AM do not reach the right balance between the ferrite and austenite phases and post-process heat treatment is needed to achieve the optimum microstructure. The time and temperature of heat treatment are determined by experimental trials.

3.3.2. Grain structure control

Among the three commonly used AM processes, PBF, DED-L, and DED-GMA, the cooling rate between the liquidus and the solidus is highest in the PBF and lowest in DED-GMA. As a result, the grain sizes are the largest in DED-GMA and the smallest in PBF. The typical grain size of parts made by PBF is smaller than 10 μm which results in good strength and ductility of the parts. Also, for a given AM process, the process variables such as heat input per unit length determine the cooling rate and the average grain size. For example, Murkute et al. [229] found that during the PBF-L of DSS 2507 an increase in the scanning speed from 100 to 1000 mm/s resulted in the decrease of the average grain size from 108 to 19 μm². During the AM of duplex steels, ferrite forms from the liquid, and its morphology depends on the ratio of the temperature gradient (G) to the solidification growth rate (R). Small values of G/R favor the formation of equiaxed grains and large values point to the formation of columnar grains. This ratio is highest in PBF and lowest in DED-GMA. Thus, the primary ferrite in duplex steels shows columnar grains in PBF and equiaxed grains in parts of duplex steels made by DED-GMA. The austenite that forms from the ferrite by solid-state phase transformation shows different morphologies depending on alloy composition and processing conditions [18] ranging from grain boundary austenite (GBA), Widmanstatten austenite (WA),

Fig. 3.3.1. (a) Microstructure of PBF-L 2507 Duplex stainless steel [222] and (b) EBSD of the microstructure showing the single-phase ferritic structure with a mosaic-type macrostructure [222].
intragranular austenite (IGA), and secondary austenite. GBA forms below 1350 °C and WA with lath morphology grows from GBA at temperatures below 800 °C. Also, IGA precipitates in the ferrite matrix when sufficient time is available [18]. The secondary austenite forms by the reheating process.

The primary ferrite grows along the building direction because the temperature gradient is maximum along this direction. The width of the ferrite grains depends on the time at high temperatures, narrow when the cooling rate is fast, and wide for slow cooling. For example, in PBF-L the width of ferrite grains is small because of the rapid cooling of 22Cr duplex stainless steel [221]. DED-GMA of a superduplex steel showed columnar ferrite with a strong [001] texture in the build direction, while the austenite had [1,101] orientations [230]. Zhang et al. reported the anisotropy of tensile properties with lower tensile strength along the vertical build direction than in the horizontal direction in ER2594 samples [230]. The anisotropy in mechanical properties due to the texture formation can be minimized by using an appropriate scanning strategy [231].

3.3.3. Control of defects

The main issues in making sound parts involve controlling the lack of fusion defects, gas and keyhole collapse porosity, residual stress and distortion, and avoiding significant changes in chemical composition. These defects have been reported in the additive manufacturing of duplex stainless steels in addition to the common issue of the need to balance the proportion of ferrite and austenite fractions mentioned in the previous section.

The lack of fusion defects is common in metallic parts made by AM. For the AM of duplex steels, the lack of fusion defects have been mitigated using higher power [223]. This experience could be anticipated since achieving an appropriate fusion zone geometry is important in ensuring adequate bonding between different layers and tacks. Previous work shows [157,232] that larger penetration compared with the layer thickness and larger fusion zone width compared with the hatch spacing are beneficial in avoiding the void space between successive layers and adjacent tracks (hatches). These geometric requirements can be achieved by enhancing heat input which is the ratio of the heat source power and scanning speed. Avoiding the lack of fusion defects improves the density of parts and in many cases avoids the expensive and time-consuming post-build hot isostatic pressing.

Gas porosity is much smaller than the lack of fusion voids and is nearly spherical being a few tens of micrometers in diameter. Their presence has been reported [223,233] during the AM of duplex stainless steels. The gas porosity results from the oxygen, nitrogen, and hydrogen dissolved in the powder and wire feedstock during their manufacture and storage, and their presence in the shielding gas during AM. Contamination of these species from the AM environment is less pronounced in PBF because of its use of a chamber where the deposition environment can be more effectively controlled than in DED-L and DED-GMA processes. The difference in the solubilities of oxygen, nitrogen, and hydrogen between the liquid and the solid alloys often results in the rejection of gases during solidification. Since the bubbles are very small and the solidification of the moving fusion zone is fairly rapid, there is commonly an insufficient time for the gas bubbles to escape from the solidifying parts. Knezovic et al. found that the porosity increased with a decrease in the interlayer temperature during the deposition of a 2205 duplex steel part [233]. Careful control of the feedstock and the part environment during AM is the most effective way of controlling the gas porosity in the part and can avoid the post-processing step.

When a high power density heat source such as a laser or electron beam interacts with an alloy, significant vaporization of alloying elements often results in a deep and narrow cavity filled with metal vapors known as a keyhole [234]. Depending on the process parameters and materials properties, the shape and size of the keyhole may change with time and the lower portion of the keyhole may collapse forming a cavity. This cavity, resulting from the instability of the keyhole, is common [235] in the PBF of alloys such as the 2205 duplex stainless steel. It is known from the literature on fusion welding that the keyhole-induced pores can be reduced by lowering the total pressure of the system [236] and by adjusting the process variables such as power and scanning speed. No systematic study has been undertaken to investigate the effects of total pressure and other process variables during additive manufacturing of duplex stainless steels.

![Fig. 3.3.2. Surface roughness of a 2205 duplex steel part deposited by PBF-L as a function of volumetric energy density](image_url)
Residual stress and distortion are major concerns for large parts made using high heat input. Among the common AM processes, the problem is most pronounced in DED-GMA and least prominent for PBF-L. The maximum residual tensile stress was reported to be 800 MPa for PBF-L of duplex steel 2205. However, the stress was reduced significantly after a heat treatment at 1000 °C for 5 min. Distortion is often controlled using reinforced supports and heat treatment is commonly used to mitigate the residual stresses. Since the literature on residual stress and distortion is scarce, and the thermophysical properties of the duplex steels are somewhat similar to the austenitic stainless steels, the existing studies on similar alloys may serve as a good starting point.

Surface roughness influences fatigue and corrosion properties and depend on process variables such as the heat source power, scanning speed, and alloy properties. For powder bed fusion, the surface roughness is relatively less pronounced and can be controlled by adjusting process variables. Fig. 3.3.2 shows the surface roughness of 2205 duplex steel parts made by PBF-L as a function of the volumetric energy density. The roughness decreases with higher energy and the results show that a relatively smooth surface may be obtained by adjusting volumetric energy density. Fast scanning contributes to the roughness by forming lines of balls rather than a continuous stream of thin molten metal layers. Thus for parts made by PBF-L, apart from high energy density, relatively low scanning speed to avoid balling would result in surfaces smooth enough to avoid post-processing. Parts made by DED-GMA and DED-L need post-processing such as machining, sand-blasting, or etching.

3.4. Other steels

This section reviews the strategies to control grain structures, phases, and defects in additive manufacturing of plain carbon steels, oxide dispersion strengthened (ODS) steels, and transformation induced plasticity (TRIP) steels. These steels are introduced below.

- Plain carbon steels are iron-carbon alloys with a small amount of Mn, Si, Cu, P, and S. These steels are further categorized based on the carbon content such as low carbon steels (<0.3 wt% C) medium-carbon steels (0.3–0.6 wt% C), and high-carbon steels (0.6–1.0 wt% C). Plain carbon steels are very popular for making structural components. However, their usage in additive manufacturing is limited because of cost considerations and the cracking susceptibility of medium and high carbon steels. A few attempts have been made to print parts of plain carbon steels using wire arc-based processes using the wires available for fusion welding and using PBF-L.

- Oxide dispersion strengthened (ODS) steels contain nano-sized oxides with excellent thermal stability that are uniformly dispersed in the iron-based alloy matrix. For example, Fig. 3.4.1 shows the presence of fine oxides of Al and Y in a part made by PBF-L. Oxides of Ti, Fe, and Cr are also common. These steels have excellent strength and high-temperature creep strength owing to the dispersion strengthening of the oxide particles as well as the solid solution strengthening of the iron-based alloy matrix. ODS steel parts are printed generally using PBF-L and DED-L methods.

- Transformation induced plasticity (TRIP) steels are high-strength steels used in the marine and automotive industries because of their excellent combination of strength and toughness. These steels contain retained austenite within a ferrite matrix that transforms into martensite when stress is applied. This unique behavior results in both high strength and toughness.

High cooling rates during AM result in very fine cellular or dendritic solidification structures in plain carbon steel parts. The size and morphology are controlled by altering the temperature gradients and cooling rates by adjusting the process parameters. Apart from adjusting the processing conditions, yttria (Y2O3) and Tellurium (Te) nanoparticles have been added to refine the grain structure during AM of ODS steels. For example, Fig. 3.4.2 (a) and (b) show that an addition of 5 wt% yttria significantly refines the grain during PBF-L. The average size of the grains is reduced from 7 ± 6 µm (Fig. 3.4.2 (a)) to 3.7 ± 3 µm (Fig. 3.4.2 (b)). Yttria nanoparticles act as potential inoculants and facilitate heterogeneous nucleation to refine the grains. High melting point tellurium nanoparticles are also used to refine the grains since they promote heterogeneous nucleation. The addition of Te narrows the grain size distribution. The range of the grain size changes from 2.5 to 25 µm to 1.5–10.5 µm. Often, Y in ODS steels forms Y2O3 which acts as a grain refiner. In addition, grain structures in additively manufactured ODS steel parts.

![Fig. 3.4.1. Nano-sized oxides formed during PBF-L of pre-alloyed ODS steel.](image-url)
are often controlled by post-process heat treatment [257,258] which adds an extra cost.

Rapid cooling during AM of plain carbon steels results in the formation of martensite. The amount of martensite is controlled by tempering the martensite using post-process heat treatment [240]. Tempering of martensite also occurs because of multiple heating and cooling cycles during the deposition of multiple layers during AM [90]. This process is often called in-situ heat treatment. The martensite formed in a deposited layer is often transformed partially or fully to tempered martensite during the deposition of subsequent layers. Tempered martensite is formed by the precipitation of nano-sized Fe₃C carbides at the carbon-enriched grain boundaries [90]. The extent of transformation of martensite into tempered martensite is affected by the local thermal cycles and thus can be controlled by adjusting the heat input, layer thickness, and scanning strategies. For example, Fig. 3.4.3 shows how to control the tempering of martensite by adjusting the heat input during PBF-L of Fe-0.45C steel [90]. Martensite is tempered due to a higher temperature at a higher heat input and forms nano-sized Fe₃C carbides at the carbon-enriched grain boundaries [90]. ODS steels have martensite and ferrite phases. However, their mechanical properties are primarily affected by the dispersed oxides that are controlled by adjusting the heat input, adding oxide-forming elements, and changing the chemical composition of the steel [250–270]. TRIP steels contain retained austenite within a ferrite matrix that transforms into martensite when stress is applied [272]. The parts often contain round or ellipsoid carbides of W, Mo, V, and Cr [272]. However, the strength and toughness depend on the extent of martensite formed when the stress is applied and thus are not largely affected by the carbide precipitates. Limited work is available in the literature on

Fig. 3.4.2. EBSD grain map micrograph of PBF-L parts of (a) SS 304L and (b) SS 304L + 5 wt% yttria [251]. The reprint permission is obtained from Dr. Joseph Beaman.

Fig. 3.4.3. Control of martensite by adjusting the heat input during PBF-L of Fe-0.45C steel [90]. (a) SEM image of un-tempered martensite in a specimen made using 60 J/mm³ volumetric heat input. (b) Higher magnification of figure (a) shows no noticeable precipitates. (c) SEM image of tempered martensite in a specimen made using 100 J/mm³ volumetric heat input. (d) Higher magnification of figure (c) shows the presence of nano-sized Fe₃C carbide precipitates.
controlling the phases in additively manufactured TRIP steel parts.

Additively manufactured plain carbon steel parts are susceptible to the lack of fusion (Fig. 3.4.4 (a)), keyhole porosity (Fig. 3.4.4 (b)), and cracking. At low heat energy input, insufficient melting results in the lack of fusion Fig. 3.4.4 (c). Keyholes are formed at a high energy density. Unstable keyholes may collapse and form keyhole pores Fig. 3.4.4 (c). Cracks form at a higher carbon content (Fig. 3.4.4 (c)). High carbon content is related to a higher alloy hardenability and a higher martensite hardness. High local hardness initiates cold cracking during cooling. These cracks propagate due to the accumulation of high stresses during cooling [241]. Fig. 3.4.4 (c) shows a process map indicating the formation of different defects at various heat energy inputs and carbon content. Such maps are immensely useful to select an appropriate combination of process parameters and alloy composition to avoid defects. Additively manufactured ODS steel parts are also susceptible to the lack of fusion [250,259] which can be controlled by increasing the heat input at a higher laser power (Fig. 3.4.5). The same strategy is also used to reduce the lack of fusion in additively manufactured TRIP steel parts [272].

4. Control of grain structure, phases, and defects in aluminum alloys

Printed aluminum alloy parts are used in the automotive, defense, and aerospace industries because of their low weight and good mechanical properties. However, there are several complexities in printing aluminum alloys. They often exhibit long columnar grains that are susceptible to solidification cracking and poor tensile properties. In addition, these parts may contain oxides and other precipitates that degrade the mechanical and chemical properties. In addition, printed aluminum alloy parts are susceptible to lack of fusion, porosity, and composition change due to selective vaporization of the alloying elements. Additive manufacturing of commonly used aluminum alloys is limited by the evolution of undesired grain structure, phases, cracking, and other defects. Therefore, printing aluminum alloy parts containing minimum defects with desired microstructure and properties is challenging. This section reviews the common strategies (Fig. 4.1) to control grain structure, phases, and defects during additive manufacturing of aluminum alloys.

Fig. 3.4.4. (a) Lack of fusion voids in Fe-0.2C part produced using PBF-L [240]. (b) Keyhole pores in Fe-0.75C part produced using PBF-L [240]. (c) Dependence of formation of different defects on heat energy density and carbon content during PBF-L of plain carbon steels. The figure is made using the data reported in [241].

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Table 4.1 provides selected examples of controlling grain structure, phases, and defects in additively manufactured aluminum alloy parts.

4.1. Strategies to control grain structure

Additively manufactured aluminum alloy parts often contain long columnar grains that are known to degrade mechanical properties and cause solidification cracking. Several control techniques are emerging to modify the long columnar grains to form small equiaxed grains as discussed below.

4.1.1. Addition of inoculants and grain refiners to achieve columnar to equiaxed transition

High melting point elements such as zirconium and scandium are added [276–279] as inoculants to promote several nucleation sites for the formation of equiaxed grains. For example, the addition of 1 vol% of zirconium in AA 7075 processed using PBF-L promoted heterogeneous nucleation resulting in small equiaxed grains [104]. The formation of equiaxed grains significantly improved the tensile properties of the part. Only 2 wt% of zirconia [280] can act as grain refiners and change the long columnar grains (Fig. 4.2 (a)) into smaller equiaxed grains (Fig. 4.2 (b) and (c)) that are beneficial for improving tensile properties [281]. Titanium and vanadium have also been used for grain refinement during AM of aluminum alloys [282].

The addition of zirconium or scandium can form Al3Zr [283,284] or Al3Sc [285–288] precipitates, respectively, from the liquid before the Al-rich primary solidification phase forms. These precipitates are known to be very effective for grain refinement during solidification by promoting heterogeneous nucleation. For example, zirconium creates two types of metastable Al3Zr precipitates. First, sub-micrometer particles form upon solidification and act as grain refining agents, nucleating fine aluminum grains that improve tensile properties. Second, Al3Zr nano-precipitates form in the solid alloy during heat treatment that precipitation-strengthen the alloy leading to a significant increase in the tensile strength over the as-fabricated value. Similar observations were also made in fusion welding [289,290]. However, the exact mechanism of the formation of these precipitates is not fully understood and more work is needed to uncover it.

Micro and nanoparticles of high melting point ceramic materials such as titanium carbide (TiC) and titanium boride (TiB2) are often added as grain refiners or inoculants during casting and fusion welding. They are also used in the additive manufacturing of aluminum alloys [291–296]. For example, TiC nanoparticles were used as grain refiners during PBF-L of pure aluminum [297], AA 7075 [296], AA 7050 [298], and AA 7475 [299].
and an Al-Cu-Ag-Mg-Ti alloy [298], DED-L of AA 5024 [299], and DED-GMA of AA 7075 [300] and AA 2219 [301]. However, the shape, size, and optimum amount of these additives are selected by experimental trials. More work is needed to examine the attributes of the additives needed to act as effective inoculants. The shape, size, and amount of the inoculant particles and their cost are important factors in the selection of inoculants.

4.1.2. Application of external vibrations to form equiaxed grains

External forces such as ultrasonic vibration and mechanical agitation can be used to change large columnar grains to small equiaxed grains that are beneficial for improving tensile properties. The mechanical vibration of the entire system has been used to break the columnar grains [302]. Thermal fluctuations in the pool could also be increased by such mechanical vibration, which could in turn increase remelting of dendrite arms at their roots. The remelted dendrite arms, if they survived, could grow into equiaxed grains and cause grain refining. The goal is to achieve many small grains (Fig. 4.3) by adjusting the amplitude and frequency of the vibration. However, the amplitude and frequency are selected based on trial and error. In addition, the efficacy of different types of ultrasonic waves (transverse or longitudinal) needs to be investigated. Plastic deformation by cold working using either mechanical hammering (or peening) [303] or laser shock peening [304] is used to produce refined grains. However, both methods interrupt the deposition process to apply the deformation and thus require longer processing times.

4.1.3. Control of cooling rates and solidification parameters

Grain morphology (columnar or equiaxed dendrites) is controlled by the ratio of the temperature gradient to the solidification growth rate. A high ratio favors the formation of columnar grains. In addition, the product of the temperature gradient to solidification growth rate represents the cooling rate during solidification which affects the fineness of the microstructure, such as the dendrite-arm spacing or cell spacing. Process conditions are adjusted to achieve the required temperature gradient and solidification growth rate to attain the desired solidification morphology and grain size. Substrate preheating and high heat input reduce the temperature gradient which is favorable for the formation of equiaxed grains. Rapid cooling at a fast scanning speed results in smaller, but more elongated, grains [305]. Inter-layer cooling can control the net heat content in the part and thus affect the temperature gradient. Decreasing power progressively during DED-GMA can reduce the heat input, enhance the cooling rate, and produce fine grains [306].
Table 4.1
Selected examples of controlling grain structure, phases, and defects in additively manufactured aluminum alloy parts.

<table>
<thead>
<tr>
<th>Objective</th>
<th>Alloy</th>
<th>AM process</th>
<th>Description of control strategy</th>
<th>References</th>
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<tbody>
<tr>
<td>Control of grain structure</td>
<td>AA 7075</td>
<td>PBF-L</td>
<td>Addition of 1 vol% Zr promoted heterogenous nucleation and resulted in equiaxed grains</td>
<td>[104]</td>
</tr>
<tr>
<td>Al-Mg-Zr alloy</td>
<td>PBF-L</td>
<td>Addition of Zr formed Al3Zr precipitates that helped in heterogeneous nucleation and formation of equiaxed grains</td>
<td>[283,284]</td>
<td></td>
</tr>
<tr>
<td>Al-Mg alloy</td>
<td>PBF-L</td>
<td>Addition of Sc formed Al3Sc precipitates that helped in heterogeneous nucleation and formation of equiaxed grains</td>
<td>[287,288]</td>
<td></td>
</tr>
<tr>
<td>Pure Al</td>
<td>PBF-L</td>
<td>Addition of TiC nanoparticles were added as grain refiners that resulted in equiaxed grains</td>
<td>[297]</td>
<td></td>
</tr>
<tr>
<td>AA 7075</td>
<td>DED-L</td>
<td>Addition of 4 wt% Si refined grains and reduced solidification cracking</td>
<td>[331]</td>
<td></td>
</tr>
<tr>
<td>AA 5024</td>
<td>DED-L</td>
<td>Post-process heat treatment reduced Mn, Cu, and Si-rich secondary phases and improved mechanical properties</td>
<td>[314]</td>
<td></td>
</tr>
<tr>
<td>AA 7075</td>
<td>DED-GMA</td>
<td>Post-process heat treatment reduced silicon-rich, globular precipitates</td>
<td>[315]</td>
<td></td>
</tr>
<tr>
<td>AA 2319</td>
<td>DED-GMA</td>
<td>Post-process heat treatment reduced Mn, Cu, and Si-rich secondary phases and improved mechanical properties</td>
<td>[314]</td>
<td></td>
</tr>
<tr>
<td>Al-5Si alloy</td>
<td>DED-GMA</td>
<td>Pulsing or arc was used to refine grains</td>
<td>[307]</td>
<td></td>
</tr>
<tr>
<td>Control of phases</td>
<td>AA 4043</td>
<td>DED-GMA</td>
<td>Post-process heat treatment reduced silicon-rich, globular precipitates</td>
<td>[315]</td>
</tr>
<tr>
<td>AA 2319</td>
<td>DED-GMA</td>
<td>Post-process heat treatment reduced Mn, Cu, and Si-rich secondary phases and improved mechanical properties</td>
<td>[314]</td>
<td></td>
</tr>
<tr>
<td>Defect control</td>
<td>AA 7075</td>
<td>PBF-L</td>
<td>Addition of grain refiners promoted columnar to equiaxed transition and reduced solidification cracking</td>
<td>[104]</td>
</tr>
<tr>
<td>AA 7075</td>
<td>PBF-L</td>
<td>Addition of 4 wt% Si refined grains and reduced solidification cracking</td>
<td>[331]</td>
<td></td>
</tr>
<tr>
<td>AA 6061</td>
<td>PBF-L</td>
<td>Substrate preheating reduced temperature gradient and stress accumulation and minimize solidification cracking</td>
<td>[345]</td>
<td></td>
</tr>
<tr>
<td>AlSi10Mg</td>
<td>PBF-L</td>
<td>Lack of fusion voids were minimized by increasing the pool size by enhancing the heat source power, decreasing the scanning speed, and reducing the hatch spacing</td>
<td>[353]</td>
<td></td>
</tr>
<tr>
<td>Al-Zr-Mg alloy</td>
<td>DED-GMA</td>
<td>Gas pores were minimized by varying the arc polarity and pulsing the arc</td>
<td>[354]</td>
<td></td>
</tr>
<tr>
<td>Al-Mg alloy</td>
<td>DED-GMA</td>
<td>Low arc current or rapid scanning resulted in low temperature and reduced composition change due to selective vaporization</td>
<td>[113]</td>
<td></td>
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</table>

![Fig. 4.2. EBSD inverse pole figure (IPF) maps of AA 2024 fabricated by PBF-L showing (a) coarse grains and showing fine grains after zirconium addition using laser scanning speeds of (b) 5 m/min and (c) 15 m/min, respectively [281].](image)
4.1.4. Other methods to control grain structure

Pulsing [307] of arc source in DED-GMA is effective at reducing the grain size. DED-GMA of aluminum alloys using cold metal transfer (CMT) technologies allows control of overall heat input which results in faster cooling and smaller dendrite arm spacings.

Fig. 4.3. Reduction in grain size with an increase in vibration acceleration during DED-GMA of aluminum-magnesium alloy with the provision for an external ultrasonic vibration source. The plot is made using the data reported in [302].

Fig. 4.4. (a) The bright-field STEM image of a printed AlSi10Mg alloy part shows the cellular structure as it forms during solidification into the fusion zone from the fusion boundary. The schematic to the right shows an overall view of the boundary structure. The characteristic layer of coarsened silicon deposits is marked with arrows that define the bottom boundary of the heat-affected zone [313]. AA 4043 parts made by DED-GMA [315] containing silicon-rich (b) globular precipitates and (c) smaller precipitates with uniform distribution after heat treatment.
Several process variants [308–312] such as conventional CMT, CMT-Pulse (CMT-P), CMT-Advanced (CMT-ADV), and CMT Pulse Advanced (CMT-PADV) can provide a progressively decreasing heat input. All the variants permit control of the current waveforms. The PADV version operates in a variable polarity mode, with cathodic cleaning of substrate oxides in the electrode positive mode. Increases in arc pressure with the variable polarity mode are claimed to cause dendrite fragmentation with subsequent formation of equiaxed grains of random texture. Further investigation is needed to provide an improved understanding of the effects of arc pressure and polarity on dendrite fragmentation.

4.2. Phase control strategies

Precipitates are the most common phases formed during the additive manufacturing of aluminum alloys. For example, rapid cooling rates during the solidification of an additively manufactured AlSi10Mg alloy [313] resulted in a small dendrite spacing in the middle of the fusion zone with uniformly distributed, nanoscale silicon-rich precipitates. The precipitates were found within the primary α-grains. A thin, distinct boundary layer containing larger α-grains and extended regions of the nanocrystalline precipitates of eutectic material was found near the fusion boundary (Fig. 4.4 (a)). Iron-rich precipitates were found to affect the mechanical properties of AA 2319 parts made by DED-GMA [314].

In-situ and post-process heat treatments are commonly used to control precipitates in additively manufactured aluminum alloy parts. For example, AA 4043 parts made by DED-GMA [315] contained silicon-rich, globular precipitates (Fig. 4.4 (b)) that are reduced by post-process heat treatment (Fig. 4.4 (c)). The heat treatment also resulted in a more uniform distribution of the precipitates. The multiple thermal cycles inherent with most AM processes provide an opportunity for in-situ heat-treating much like that experienced during temper bead welding during arc welding. The effects of multiple thermal cycles during AM processes are referred as intrinsic heat-treating. For Al alloys that are precipitation strengthened, this approach would require either very fast cooling of each pass after solidification to keep solute in solution or subsequent thermal cycles that reach temperatures high enough to re-solutionize. Note that the choice of process parameters to provide these thermal cycles must also yield fully dense deposits without defects. One method for developing a set of parameters to meet all the requirements is process simulation. In addition, post-process heat treatments to dissolve unwanted phases or to provide spheroidization of features for improved mechanical properties are possible for AM of Al alloys. However, post-process heat treatment adds extra cost.

4.3. Control of common defects

Additively manufactured aluminum alloy parts are susceptible to common defects such as cracking, lack of fusion, porosity, and composition change. For example, AA 2139 parts suffered from evaporative loss of magnesium that significantly reduced the hardness [316]. Elongated pores due to lack of fusion were observed in printed AA 1100 parts [317]. Al 5083 parts made by DED-L exhibited gas porosity, evaporative loss of magnesium, and the presence of pure magnesium HCP phase surrounded by a matrix of FCC aluminum, all of which affected the structure and properties of parts [318]. AlSi10Mg parts made by PBF-L have been found to have defects such as porosity that degrade the mechanical properties [319–321]. Porosity was also observed in aluminum alloys 1100, 4043, 4943, 4047, and 5356 parts made by DED-GMA [322]. This section reviews commonly used control strategies to mitigate these defects in additively

![Fig. 4.5.](image)
manufactured aluminum alloy parts.

4.3.1. Solidification cracking

Solidification cracks are often visible in the fusion zone, along grain boundaries, and the fracture surfaces show dendrites or cells [103]. Significant progress has been made in understanding solidification cracking in casting and fusion welding of aluminum alloys that are also applicable for additive manufacturing [323,324]. A simple index \( |dT/d(f_s)^{1/2}| \) was used to evaluate the susceptibility to solidification cracking [325], where \( T \) is temperature and \( f_s \) is the fraction of solid. It was suggested that the maximum \( |dT/d(f_s)^{1/2}| \) up to \( (f_s)^{1/2} = 0.99 \) (i.e., \( f_s = 0.98 \)) is a convenient option for the index. This is because the maximum \( |dT/d(f_s)^{1/2}| \) usually occurs near \( (f_s)^{1/2} = 1 \) and because beyond \( f_s = 0.98 \), the grains can bond to each other extensively to resist cracking [326]. Commercial thermodynamic software and database can be used to calculate the \( T \) versus \( (f_s)^{1/2} \) curves and obtain values of \( |dT/d(f_s)^{1/2}| \). For instance, “Pandat” [327] and “PanAluminum” commercial packages [328] can be used to calculate the index of an Al alloy based on its composition. It is interesting to note that the crack susceptibility of one alloy relative to a similar alloy different in composition in arc welding has been found similar to that in laser- or electron-beam welding [329]. For example, the crack-susceptibility ranking of 6061 Al > 7075 Al > 2219 Al observed in arc welding was also observed in electron-beam welding. Both back diffusion and reactions that consume the interdendritic liquid can help resist solidification cracking. They can increase \( f_s \) at a given \( T \) to flatten the \( T-(f_s)^{1/2} \) curve and hence significantly reduce \( |dT/d(f_s)^{1/2}| \). This mechanism has been verified in different Al alloys.

The Al-Mg alloy system, based on its low eutectic temperature \( (T_E = 450 \, ^\circ C) \), can be expected to be significantly more susceptible to solidification cracking than the Al-Cu alloy system \( (T_E = 548 \, ^\circ C) \). Indeed, the much lower \( T_E \) of Al-Mg alloys makes its \( T \) versus \( (f_s)^{1/2} \) curves much steeper, suggesting a higher crack susceptibility. However, Fig. 4.5 shows that 5086 Al (−Al-4 Mg) resists solidification cracking much better than 2014 Al (−Al-4.4Cu) [330]. Liquid Wood’s metal at 75 \( ^\circ C \) was poured from a glass beaker onto the weld pool and its surroundings to freeze and capture the elevated-temperature microstructure of the mushy zone and simultaneously induce transverse tension in it to cause cracking. In 2014 Al, continuous interdendritic liquid films exist as easy paths for intergranular cracking but not in 5086 Al. The much higher maximum solubility of Mg in solid Al (17.5 wt% Mg) than Cu in solid Al (5.65 wt% Cu) encourages much Mg back diffusion into Al-rich dendrites to deplete the interdendritic liquid. This is consistent with the dramatic flattening of the \( T \) versus \( (f_s)^{1/2} \) curves of Al-Mg alloys and a significant reduction in both \( |dT/d(f_s)^{1/2}| \) and crack susceptibility [330].

In commercial Al alloys, Si, Cu, Mg, Zn, and Li are common alloying elements. Al-Si alloys, including AlSi10Mg, have low susceptibility to solidification cracking. Al-Si alloys are widely used in casting, with excellent castability due to their narrow freezing temperature range (a high eutectic temperature of 577 \( ^\circ C \)) and good fluidity (high fraction of eutectic). Hyer et al. [102] investigated solidification cracking in PBF-L of Al-Si alloys, including six binary Al-Si alloys and AlSi10Mg and Al12Si. Only Al-Si alloys with 1.0 and 2.0 wt% Si were found to exhibit solidification cracking, consistent with the prediction based on the index \( |dT/d(f_s)^{1/2}| \). The addition of silicon can prevent cracking in aluminum alloys by increasing the fraction eutectic that forms and reducing the

Fig. 4.6. Liquation cracking vs. solidification cracking in bead-on-plate, gas-metal arc weld of 6061 Al [347].
solidification temperature range. In some aluminum alloys such as AA 2024 and AA 7075, silicon addition can result in precipitation hardening to achieve high strengths. However, the amount of silicon is significantly less than that used for casting and filler metal in welding to minimize cracking. For example, the addition of 4 wt% of silicon in AA 7075 during PBF-L resulted in fine grains at the fusion boundary more likely due to epitaxy and competitive growth [331]. A new alloy composition with 6.5 wt% of silicon was developed by mixing AA 7068 powders with Al10SiMg which was found to minimize cracking [332]. Selection of process parameters [333–335], scan strategy [336], and modeling [337] to understand and reduce solidification cracking during PBF-L of aluminum alloys have been demonstrated.

The most effective control of solidification cracking is to avoid the composition range of the highest crack susceptibility. For a binary Al alloy system (e.g., Al-Si, Al-Cu, Al-Mg, or Al-Li) the crack susceptibility curve can be used as a guide, which shows the crack susceptibility as a function of the solute content. The composition range near the solute content corresponding to the highest crack susceptibility should be avoided. For a ternary (e.g., Al-Mg-Si, Al-Cu-Mg, or Al-Cu-Si) or quaternary (e.g., Al-Si-Mg-Cu, Al-Zn-Mg-Cu or Al-Li-Mg-Cu) Al alloy system, a crack susceptibility map can be used as a guide to avoiding the composition range of the highest crack susceptibility. Crack susceptibility curves or maps have been determined experimentally for Al alloys. They also have been calculated based on the index |dT/d(fS)1/2|, including binary [338,339], ternary [340], and quaternary [100] Al alloy systems and verified against experimental results. New alloys are being developed to reduce cracking during additive manufacturing [341,342].

If high-strength Al alloys with compositions susceptible to solidification cracking [343,344] have to be used for AM, grain refining should be considered. Reduction of cracking during solidification by grain refining has been demonstrated in casting [345] and welding of Al alloys. In powder bead fusion of 6061 Al, preheating of the powder bed has been shown to eliminate solidification cracking [346]. Preheating reduces the temperature gradients and thermally induced tensile stresses and solidification cracking.

**Fig. 4.7.** (a) An increase in hatch spacing results in more lack of fusion voids and decreases part density during PBF-L of AlSi10Mg [353]. (b) Evolution of lack of fusion voids with scanning speeds (I) 250 mm/s, (II) 500 mm/s, (III) 750 mm/s, and (IV) 1000 mm/s during PBF-L of AlSi10Mg [353].
Substrate preheating was effective to reduce cracking in PBF-L of AA 6061 by reducing the temperature gradient and accumulated stress [345]. Different scanning strategies were used to attain desired cooling rates and solidification parameters to control microstructure and reduce cracking in AM of aluminum alloys [346]. Significant progress has been made to mitigate the solidification cracking by controlling the solidification morphology, designing new alloys, and making changes in the additive manufacturing process. In addition to the persistent problems of solidification cracking, AM of aluminum alloys also suffer from other defects as explained below.

4.3.2. Liquation cracking

Liquation cracking occurs in the partially melted zone (PMZ) of an alloy, where localized liquid formation (i.e., liquation) occurs along grain boundaries as well as at isolated spots within grains. Fig. 4.6 compares solidification cracking and liquation cracking in a 6061 Al weld [347]. Both are intergranular. However, the fracture surface is dendritic with the former but smooth with the latter. Liquation cracking can occur if the PMZ is under significant tension, e.g., by the solidifying/contracting mushy zone nearby. Alloys with a wider freezing temperature range are more crack susceptible. In arc welding, a suitably designed filler metal can be used to eliminate liquation cracking. A simple criterion was proposed by Kou and coworkers and verified experimentally. It states that cracks occur if the weld-metal $f_S >$ base-metal $f_S$ after $f_S$ reaches about 0.3. This criterion has been verified for Al and Mg alloys [111,112,348]. In some systems, water cooling was found to reduce liquation cracking [349]. It was suggested columnar grains grew more nearly

![Fig. 4.8. Gas porosity during wire arc additive manufacturing of an Al-Zn-Mg alloy using cold metal transfer with (a) varying polarity, (b) fixed polarity, (c) varying polarity with arc voltage pulsing, and (d) fixed polarity with arc voltage pulsing [354].](image-url)
vertically upward with water cooling, and this reduced the grain-boundary angle and hence the undercooling of the grain boundary liquid. In welding, the explanation can be straightforward, that is, water cooling reduces the extent of liquation and hence liquation cracking. The Laves/γ eutectic can remain liquid well below the liquidus temperature (~1355 °C), e.g., 1000 °C [350], thus allowing liquid films between grains to persist to promote both solidification and liquation cracking.

4.3.3. Lack of fusion and porosity

Additively manufactured aluminum alloy parts are susceptible to the lack of fusion voids and porosity both of which significantly degrade the mechanical properties of the parts [351,352]. Improper fusion adherence among the neighboring tracks results in the formation of lack-of-fusion voids [351,352]. Moisture from the atmosphere and the gas entrapped inside the gas-atomized powders often cause gas porosity inside the component [351,352]. Gas pores are spherical and their size is much smaller (<20 µm) than the typical lack of fusion voids. In contrast, the lack of fusion pores are often irregular in shape and often they are much bigger than the gas pores [274].

Lack of fusion is affected by the extent of overlap between two consecutive tracks. The extent of overlap between tracks can be controlled by adjusting the molten pool size and the distance between two neighboring tracks. A high hatch spacing that indicates more distance between two neighboring tracks reduces the overlap between two tracks [353] and increases the lack of fusion voids (Fig. 4.7 (a)). Parts made with small hatch spacing can reduce the lack of fusion voids but it needs more number of hatches to be deposited which decreases the productivity. Therefore, an estimation of an optimum hatch spacing is needed that reduces the lack of fusion voids without significantly affecting productivity. A selection of an optimum hatch spacing is often done by time-consuming and expensive experimental trials or by using mechanistic models. For the same hatch spacing, the lack of fusion voids can be reduced by increasing the pool size by increasing the heat source power or decreasing the scanning speed [353]. For example, the amount of lack of fusion voids during PBF-L of AlSi10Mg can be reduced (Fig. 4.7 (b)) by decreasing the scanning speed [353]. However, increasing heat input for reducing the lack of fusion voids may cause other issues such as distortion or accumulation of high residual stresses.

Aluminum alloys often react with moisture and produce hydrogen gas that is entrapped inside the molten pool and results in gas pores [274]. Moisture content can be reduced by drying up the powders by preheating. Therefore, preheated powders often show less gas porosity in parts. However, preheating powders adds an extra step and increases production costs. Since Zn has a low boiling point, additively manufactured parts of Al-Zn-Mg alloys such as high-strength 7xxx aluminum alloys often contain gas pores of Zn vapors (Fig. 4.8). These alloys are often used to print structural components using wire arc additive manufacturing where pores are reduced [354] by varying the arc polarity and pulsing the arc (Fig. 4.8). However, the exact mechanism of how pulsing and varying polarity reduces gas pores is not fully understood and needs further research. In addition, since aluminum alloys have low yield strength, gas pores often initiate cracks under high solidification stress [355]. Reduction of lack of fusion voids and gas pores in additively manufactured aluminum alloy parts remains an important challenge to improve the mechanical properties of parts. Post-process hot isostatic pressing can reduce the voids but adds an extra cost.
4.3.4. Composition change due to selective vaporization of alloying elements

Aluminum alloys often contain magnesium, zinc, copper, manganese, silicon, and some other elements in small quantities. These elements have very different vapor pressures. Therefore, they vaporize at different rates from the molten pool depending on their concentration and vapor pressure over the alloy. This selective vaporization of different alloying elements results in a change in the composition of the part from the feedstock \([113,316,318,356,357]\). Composition change can degrade the microstructure and corrosion resistance and may cause defects such as cracking.

The Fig. 4.9 (a) shows the composition change of major constituting elements during DED-EB of aluminum 2139 alloy \([316]\). Mg shows the maximum change in composition for the aluminum alloy considered. Similarly, depletion of magnesium \([358]\) in the weld zone in bead-on-plate autogenous conduction mode laser welding of thin aluminum alloy 5182 plates (4.2 wt% Mg, 0.2%Si, 0.35% Mn, 0.07% Zn, 0.15%Cu, 0.1% Ti and balance Al) can be observed in Fig. 4.9 (b). These results indicate that relatively low boiling point elements, such as Mg, and Zn, selectively vaporize out of the molten pool more readily than other elements. The vaporization rate depends on the temperature distribution on the surface of the fusion zone. Reducing the temperature by reducing power or increasing speed can alleviate the severity of composition change. For example, Fig. 4.9 (c) and (d) indicate that loss in Mg during wire arc additive manufacturing of an aluminum alloy can be significantly reduced by reducing the arc current or by scanning faster \([113]\).

5. Control of grain structure, phases, and defects in nickel alloys

5.1. Polycrystalline nickel alloys

A variety of polycrystalline parts of nickel-base alloys have been printed by fusion-based additive manufacturing processes. These alloys can be organized into three categories \([359]\): solid-solution strengthened alloys containing various substitutional elements such as Cr, Fe, Mo, Nb, and W, precipitation strengthened alloys containing precipitate forming elements such as Ti, Al, and/or Nb that form strengthening precipitates such as \(\gamma'(\text{Ni}_3\text{Ti}, \text{Al})\) and \(\gamma''(\text{Ni}_3\text{Nb})\), and specialty alloys such as NiTi with shape memory effect and Ni-15Fe-5Mo with unique magnetic properties. The precipitation-strengthened alloys are further divided into two groups based on their welding capabilities \([359]\): weldable (e.g., Inconel 718 and Hastelloy X) and unweldable (e.g., CM247LC). This section is focused on the AM of solid-solution and precipitation strengthened nickel alloys. Detailed information on AM of shape memory and magnetic materials may be found in recent review articles by Elahinia et al. \([360]\) and Chaudhary et al. \([361]\), respectively.

Table 5.1 highlights selected literature articles on AM of various nickel alloys. INVAR, technically a Fe base alloy, is included since the solidified matrix phase is also FCC (\(\gamma\)-austenite). While sharing the same layer-by-layer printing approach, there are significant differences in the different AM processes \([362–375]\) shown in Table 5.1. Particularly, due to the need for lightly sintering each layer of

<table>
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<tr>
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<th>AM process</th>
<th>Salient features of the as-built microstructure</th>
<th>Reference</th>
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<tr>
<td>Inconel 625</td>
<td>PBF-EB</td>
<td>Columnar grains parallel to the build direction; thin (\gamma') precipitates</td>
<td>([364])</td>
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<tr>
<td>Inconel 625</td>
<td>PBF-L</td>
<td>Columnar grains with strong ((001)) texture; no carbides or other precipitate phases detected by XRD or SEM</td>
<td>([365])</td>
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<tr>
<td>Inconel 625</td>
<td>DED-L</td>
<td>Columnar dendrites which grew epitaxially from the substrate; no precipitates detected by XRD or SEM</td>
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<td>Hastelloy C-276</td>
<td>DED-GTA</td>
<td>Columnar dendrites; (P) (rho) phase precipitates</td>
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<tr>
<td>INVAR (Fe-36 wt % Ni)</td>
<td>PBF-L</td>
<td>Columnar (\gamma) grains grown epitaxially beyond several layers with texture near ((001)); nanosized (\alpha) precipitates</td>
<td>([367])</td>
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<td>Inconel 718</td>
<td>PBF-EB</td>
<td>Columnar to equiaxed transitions by rapidly changing the electron beam heat source between point and line heating</td>
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<tr>
<td>Inconel 718</td>
<td>PBF-L</td>
<td>Fine columnar dendrites; precipitates comprising mostly Laves phase along with a small amount of NbC carbide</td>
<td>([409])</td>
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<tr>
<td>Inconel 718</td>
<td>DED-L</td>
<td>Columnar grains with high heterogeneity; (\gamma') precipitates formed at the bottom region of the build due to repeated heating and cooling</td>
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<tr>
<td>Hastelloy X</td>
<td>PBF-L</td>
<td>Columnar grains; nanoscale precipitates enriched in Al, Ti, Cr, and O</td>
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<tr>
<td>Hastelloy X</td>
<td>PBF-EB</td>
<td>Columnar grains with a strong texture in ((001)) direction; Mo-rich MoC and Cr-rich Mo2C carbides</td>
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<td>Hastelloy X</td>
<td>DED-GMA</td>
<td>Columnar grains near the substrate transitioned into cellular grains higher in the bead; Mo carbide</td>
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<tr>
<td>Haynes 282</td>
<td>PBF-L</td>
<td>Columnar grains aligned with the build direction; ((\text{Ti}, \text{Mo})) carbide particles, and no (\gamma') precipitates detected</td>
<td>([372])</td>
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<tr>
<td>Haynes 282</td>
<td>DED-L</td>
<td>Columnar dendrites; ((\text{Ti}, \text{Mo}), \text{C}), and Mo-rich (\text{Mo}_2\text{C}) precipitates</td>
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<tr>
<td>Nimonic 263</td>
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<td><strong>Unweldable precipitation strengthened alloys</strong></td>
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<td>Inconel 713LC</td>
<td>PBF-L</td>
<td>Columnar grains oriented in the build direction with some equiaxed grains on the upper surface; Cracks due to solidification cracking and ductility dip cracking</td>
<td>([414])</td>
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<tr>
<td>Inconel 738LC</td>
<td>PBF-L</td>
<td>Columnar grains with a preferential alignment of ((001)) along the build direction; very fine carbide and (\gamma') precipitates</td>
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<tr>
<td>CM247LC</td>
<td>PBF-L</td>
<td>Fine, columnar grains with the preferential alignment of ((001)) along the build direction; fine MC carbides and very fine (\gamma') precipitates; cracking particularly near the periphery of the samples</td>
<td>([373])</td>
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<tr>
<td>Rene 142</td>
<td>PBF-EB</td>
<td>Columnar grains; cuboidal (\gamma') with volume fraction of 59%, and HfC precipitates; cracks observed</td>
<td>([374])</td>
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<tr>
<td>CMSX-4</td>
<td>PBF-EB</td>
<td>Polycrystalline, columnar grains; cuboidal (\gamma') with volume fraction of 72%</td>
<td>([363])</td>
</tr>
<tr>
<td>CMSX-4</td>
<td>PBF-L</td>
<td>Polycrystalline, columnar grains; small Laves precipitates enriched in Re, W, and Ta, and no (\gamma') precipitates detected by SEM; cracks observed</td>
<td>([375])</td>
</tr>
</tbody>
</table>
powder before melting, PBF-EB “inherently” operates with a high preheat, making it suitable to mitigate cracking issues. Such high-temperature preheating is not common for the other AM processes. The heat input in PBF-L, DED-L, and DED-GMA generally increase, resulting in a larger molten pool and lower cooling rate [3,4].

The existing literature on AM of nickel alloys has the following common features.

(i) The matrix phase, \( \gamma \), tends to solidify in the form of fine, columnar dendrites. Such grain morphology results from the local solidification conditions. Fusion-based AM processes, especially PBF-L and PBF-EB, are characterized by very localized melting (e.g., molten pool having a width of the order of 0.1 mm) and fast travel (e.g., travel speed of the order of 1 m/s). Consequently, both the solidification rate (\( R \)) and the temperature gradient at the liquid/solid interface (\( G \)) are very high [3,4]. As shown in Fig. 5.1(a), the combination of high \( R \) and \( G \) results in columnar dendrites. Moreover, the scale or size of columnar grains decreases as the product of \( G \) and \( R \), which corresponds to the cooling rate, increases. The high \( R \) and \( G \) values in PBF AM thus lead to fine dendrites with a primary dendrite arm spacing of the order of 1 \( \mu \)m.

(ii) Commonly, the as-built microstructure in PBF processes has a strong texture with the \( \langle 001 \rangle \) direction aligned with the build direction. The solidification process during AM of nickel alloys is dominated by epitaxial growth from the substrate or the previously deposited layer. During the epitaxial growth, the dendrites for which the easy growth directions (i.e., \( \langle 001 \rangle \) for FCC metals) are aligned with the maximum heat flow direction are favored. As shown in Fig. 5.1(b), the molten pool for PBF has the appearance of a flat tail where the maximum heat flow direction is vertically aligned with the build direction due to the fast travel speed [3,4]. As a result, dendritic grains oriented in \( \langle 001 \rangle \) directions grow vertically resulting in a strong texture. On the other hand, the molten pool for DED has a more curved tail, and as a result, the grains grow in an inclined direction.

Fig. 5.1. (a) solidification map of IN718 superimposed with representative \( G \) and \( R \) values during solidification in PBF-L [4,383], (b) schematic illustration of dendrite growth directions in the central longitudinal plane during PBF versus DED [3], and (c) concentration profile of Nb from dendrite core to inter-dendritic region due to micro-segregation [376].
(iii) Micro-segregation is prevalent due to non-equilibrium solidification. An example [376] of the segregation of Nb from the dendrite core to the inter-dendritic region in an as-built IN718 is shown in Fig. 5.1(c). In addition to Nb, alloying elements such as C, Ta, and Al tend to segregate into the inter-dendritic region. Such micro-segregation results in the formation of carbides and topologically close-packed (TCP) phases such as Laves.

(iv) Whether or not the strengthening precipitates ($\gamma'$ and $\gamma$) formed in the as-built microstructure depends on the local temperature experienced by the material. Due to the low preheat and rapid cooling in PBF-L, a discernable amount of $\gamma'$ or $\gamma$ is generally not formed. On the other hand, in-situ “aging” can occur due to high preheat in PBF-EB or significant heat build-up in DED-L, resulting in the formation of $\gamma'$ or $\gamma$.

(v) Compared with fusion welding, cracking issues in unweldable precipitation strengthened alloys printed by AM are generally less due to the low heat input and resulting fine microstructure and high preheat in PBF-EB.

The as-built microstructure and defects result from the complex interactions of materials and processing conditions. Detailed information on the mechanical properties of nickel alloys printed by PBF can be found in a recent review article by Sanchez et al. [377]. Strategies to improve the build quality in terms of grain structure, phases, and defects are reviewed here.

5.1.1. Strategies to control grain structure

5.1.1.1. Control spatial distribution of solidification conditions. The solidification mode can be altered by adjusting the local solidification conditions especially $G$ and $R$. For PBF-EB of IN718, a transition from columnar to equiaxed solidification mode was achieved by rapidly changing the electron beam heat source between point and line heating [378–380]. As shown in Fig. 5.2, the solidification map is superimposed with the $G$ and $R$ values calculated using a fast analytical solution to the heat conduction equation. Most points in Region 1 where the processing parameters minimized the solidification cooling rate fell within the $G$-$R$ space for equiaxed solidification mode. On the other hand, Region 2 where the cooling rate was maximized had more points in the columnar morphology zone. The grain structure for both regions corroborated well with the experimental data. Similarly, by controlling the local solidification conditions in the $G$-$R$ space such as in the product form of $G^{-m}R^{-n}$ (where $m$ and $n$ are material parameters), Raghavan et al. [381] were able to alter the primary dendrite arm spacing from 4 to 10 $\mu$m using spot melt scanning patterns in PBF-EB of IN718. Rather than utilizing the spot melting, Helmer et al. [382] showed that the grain refinement was observed in PBF-EB of IN718 when the travel speed was increased and the hatch spacing was reduced correspondingly. Additionally, by altering electron beam power and scanning speed in PDB-EB of IN718, Ding et al. [379] were able to achieve the as-built microstructure ranging from fully columnar grains to mixtures of columnar and equiaxed grains.

As mentioned previously, the common as-built microstructure in PBF of nickel alloys is columnar grains with a strong texture [383–385]. The strong texture can lead to severe anisotropy in mechanical properties [3], which is generally undesirable for structural applications. The laser scanning strategy has been varied to control the size and texture of the grains. Keshavarzkermani et al. [383] investigated the effect of four laser scanning patterns on the as-built microstructure of Hastelloy X printed by PBF-L. Fig. 5.3(a) shows two of the scanning strategies: Stripe Uni and Stripe Rot. The former resulted in the largest average grain size of 734 $\mu$m and the strongest texture due to repetitive heat flow patterns created in the successive layers. On the other hand, Stripe Rot scanning resulted in the smallest average grain size of 85 $\mu$m and the most randomly distributed texture due to the highest randomness in the heat flow directions [383]. Similar work was recently reported by Nadammal et al. [385] where the effect of four laser scanning patterns on the as-built microstructure of IN718 printed by PBF-L was studied. They also found that the 67° rotational strategy, similar to the Stripe

![Fig. 5.2. The transition from columnar to equiaxed solidification mode achieved by controlling the spatial distribution of solidification conditions during PBF-EB of IN718 [378].](image-url)
Rot in [383] weakened the texture by forming finer microstructural features.

For PBF-L of IN738LC, an unweldable nickel alloy, Geiger et al. [386] studied scanning strategies with three different rotation angles: 90°, 45° and 67°. On a plane parallel to the build direction, all three rotation angles resulted in columnar grains with strong \(001\) texture aligned with the build direction. On a plane perpendicular to the build direction, the scanning strategy with 67° rotation angle resulted in a uniform mixture of grains with \(001\) and \(011\) orientations, whereas the 90° and 45° rotation angles resulted in grains with predominately \(001\) orientation.

Unlike the above studies on PBF-L [383–389] where the laser power was held constant, Popovich et al. [390] studied PBF-L of IN718 printed with two laser powers: 250 and 950 W. As expected, the high laser power resulted in much coarser columnar grains than...
the lower laser power. An interesting part of their study is the printing of the graded sample where different parts along the built height were printed with a laser power of either 250 or 950 W, resulting in a sharp transition in the microstructure.

The effective laser power was altered by using a pulsed laser instead of a continuous wave laser in the DED-L of IN718 by Xiao et al. [391]. The pulsed laser resulted in a refined dendrite microstructure, which was attributed to a faster cooling rate and shorter solidification time of the molten pool. For the DED-L of IN718, Dinda et al. [392] studied the effect of laser beam scanning patterns on dendrite growth morphology. As shown in Figure 5.3(b), the unidirectional laser beam scanning pattern developed a strong \( \langle 001 \rangle \) texture that was inclined at 30° to the build direction and 60° with the scanning direction. On the other hand, a backward and forward scanning pattern developed a rotated cube texture. The bidirectional scanning strategy breaks the long columnar grains and results in a zig-zag pattern of the orientation of the primary dendrites with about 15° misorientation with the primary heat flow direction [156]. As described earlier, the formation of different textures is largely affected by how well dendrites with \( \langle 001 \rangle \) orientation are aligned with the maximum heat flow direction [3].

5.1.1.2. Formation of equiaxed grains by adding inoculants. The addition of inoculants or grain refiners represents a metallurgical approach to increase the number of nucleation sites and thus new grains. A variety of inoculants have been tested for grain refinement in additively manufactured nickel alloys. The inoculants can be divided into the following three groups.

The first group is yttria (\( \text{Y}_2\text{O}_3 \)), which is the primary strengthening agent utilized in a special class of nickel alloys known as oxide dispersion strengthened (ODS) nickel alloys. Tan et al. [393] studied DED-L of an ODS nickel alloy where the nickel alloy powder (Ni-21Cr-0.85Fe-0.57Ti-0.25Al by wt.%) was mechanically alloyed with 0.6 wt% \( \text{YH}_2 \) powder. During the high-energy mechanical alloying process, Y and O dissolved into the powder. Dispersed oxides in the form of Y-O and Al-O oxide cores surrounded by Cr-rich shells were generated after DED-L although the oxide’s size and number density were larger than those in a reference material prepared by the standard hot extrusion process using the same mechanical alloyed powder. Additionally, the as-built microstructure mainly comprised columnar dendrites growing along the build direction. When compared to another DED-L sample using nickel alloy powder without mechanical alloying, the oxides formed in DED-L with mechanically alloyed powder refined the columnar grains. Kenel et al. [394] mechanically alloyed a Ni-Cr-Al-Ti model alloy powder with 0.5 to 1 wt% \( \text{Y}_2\text{O}_3 \) nano-powder, and the alloyed powder was printed by PBF-L. It was observed that most \( \text{Y}_2\text{O}_3 \) dispersoids were consumed by processes such as reaction with Al or \( \text{Al}_2\text{O}_3 \) to form a liquid \( \text{Y}_4\text{Al}_2\text{O}_9 \) slag. Nevertheless, some of the added \( \text{Y}_2\text{O}_3 \) dispersoids were successfully distributed through the solidified matrix as nano-dispersoids without coarsening, noticeably reducing grain size compared to the unmodified base alloy. Additional information on AM of oxide-dispersion strengthened nickel alloys may be found in a recent review article by Wilms [395].

The second group of added inoculants is various ceramic particles, resulting in the formation of metal matrix composites after printing. Ghodsi et al. [396] used a powder decoration method to produce composite IN625 particles with submicron yttria-stabilized
zirconia (YSZ) particles uniformly distributed on the surface. Compared to the unmodified IN625, the YSZ added IN625 resulted in the formation of small grains, thus supporting the role of YSZ as a nucleation agent. TiC particles were added to Inconel 625 for DED-L by Hong et al. [397], IN718 for PBF-L by Gu et al. [398], and Hastelloy X for PBF-L by Han et al. [399]. All those studies used ball milling or high-speed mixing to “coat” the nickel alloy powder with nanoparticles of TiC. After printing, TiC particles were found to be uniformly dispersed along the grain boundaries and inside the grains, and grain refinement was observed in the nickel alloys added with TiC. TiB2 particles were added to Hastelloy X for PBF-L by Yang et al. [400] and to Inconel 625 for DED-L by Zhang et al. [401]. Grain refinement was observed in the former but absent in the latter; the difference is likely caused by the different heat input and alloy composition used in those two studies.

The third group of added inoculants is based on carbon. Wang et al. [402] coated IN625 powder with multi-walled carbon nanotubes (MWCNTs), and the coated powder was used to print rectangular bars by PBF-L. A very low concentration of MWCNTs was observed inside the γ matrix. Moreover, there was a significant enrichment of Mo and Nb around the MWCNT, indicating the formation of carbides on the boundary between MWCNT and the metal matrix. Nevertheless, the addition of MWCNTs resulted in grain refinement for IN625. In another study by Chen et al. [403], the powders of precipitation strengthened nickel alloy K418 were coated with graphene nanoplatelets (GNPs) by plasma-assisted ball milling and then printed by PBF-L. It was found that the majority of GNPs were uniformly dispersed within the γ grains. The columnar grains of the as-built K418 sample were transformed into approximately equiaxed grains by the addition of GNPs.

5.1.1.3. Modification of alloy composition. Kong et al. [404] studied the effect of Nb on the grain size for IN718 printed by DED-L. A dual-feed system was used to deliver a mixture of two IN718 powders: one containing 1.0 wt% Nb and the other containing 8.0 wt% Nb. By controlling the delivery rate of each powder, the Nb content of the fabricated samples was varied. It was found that the grain size rapidly decreased from 300 μm to 70 μm as the Nb content increased from 1 to 6 wt%. The grain refinement was attributed to the solute drag or pinning effect of Nb as well as increased nucleation sites with a higher amount of Nb.

5.1.1.4. Breaking up long columnar grains by external agitations. The application of high-intensity ultrasound to the liquid metal for refining the solidification grain structure is well studied in the casting and welding literature [405]. A key mechanism for grain refinement is the acoustic cavitation process during which bubbles are created. When a bubble collapses, intense, localized shock waves are emitted, fracturing the already solidified dendrites. The fractured dendrite pieces are carried away by the acoustic stream and serve as heterogeneous nuclei, promoting the formation of fine equiaxed grains.

Todaro et al. [273] deposited IN625 powder by DED-L onto a 4140 stainless steel substrate (sonotrode) that was vibrating at 20 kHz along the build direction. A substantial reduction in grain size was observed in the deposit with ultrasonic vibration when compared to the standard one without ultrasound. The effect of ultrasonic vibration on IN718 printed by DED-L was studied by Wang et al. [406]. The part was deposited also on a substrate that vibrated along the build direction. Three ultrasound frequencies, 25, 33, and 41 kHz, were evaluated. The grain size was reduced from 7 μm at 25 kHz to 4 μm at 41 kHz and the aspect ratio was decreased as well.

5.1.1.5. Comparison of different grain structure control approaches. Following the classification scheme used in [390], the existing approaches for controlling the solidification grain structure can be divided into three categories: thermal, metallurgical, and mechanical. The thermal approach largely relies on the manipulation of processing parameters to control the spatial variation of solidification conditions (e.g., G and R) and consequently the extent of columnar versus equiaxed grains. The advantage of the thermal approach is that they are readily implementable and can be applied to different materials. On the other hand, the extent of control can be limited especially for PBF-L and DED processes. Even for PBF-EB which offers high flexibility in controlling G and R, the scanning strategies developed on simple geometries may produce different grain structures when printing complex geometries [407].

The addition of inoculants or modification of alloy composition represents the metallurgical approach toward controlling the grain structure. Such an approach can be very effective in refining the grain structure. However, coating the nickel alloy powder with the desired inoculant is commonly done through an elaborate process such as ball milling. Moreover, the addition of inoculants into the molten pool can increase the formation of defects. Modification of alloy composition [387,404,408] can result in a nickel alloy whose composition falls outside of the industry specification. For example, the standard specification for IN718 limits Nb plus Ta to 4.75 to 5.50 wt% [387]. The study by Kong et al. [404] had an Nb concentration from 1.0 to 6.0 wt%.

Introducing ultrasonic vibration to the molten pool represents the mechanical approach to controlling the grain structure. This approach can be highly effective and does not require any modification to the alloy metallurgically. However, additional equipment is needed. Moreover, the existing studies in [273,380,406,409] printed small samples on a substrate that was vibrating ultrasonically. Scaling up this approach to large and heavy parts would require further study.

5.1.2. Phase control strategies

As shown in Table 5.1, the as-printed phases of nickel alloys include the FCC (γ) matrix phase and various precipitates such as carbides, Laves, γ' and γ". The formation of carbides and Laves is largely affected by the non-equilibrium solidification process, especially micro-segregation of alloying elements into the interdendritic region. For example, for the most frequently studied alloy in AM, IN718, Laves phase, a topologically close-packed phase with a nominal composition of Ni3Nb, is ubiquitously present in the as-printed microstructure due to the Nb segregation into liquid during non-equilibrium solidification. These precipitates are commonly observed at the interdendritic regions or grain boundaries as they form near the final stage of solidification. The carbides formed range from NbC in IN718 [409], (Ti, Mo)C in Haynes 282 [372,393,394], Mo-rich M6C and Cr-rich M23C6 in Hastelloy X [370], to HfC in...
Rene 142 [374]. On the other hand, the formation of strengthening precipitates $\gamma'$ and $\gamma''$ via solid-state phase transformation, is largely affected by the preheating or heat build-up in the part. In addition to these precipitates, the as-printed microstructure has been found to contain oxide inclusions due to the reaction of alloying elements particularly Al with the oxygen in the build chamber in both PBF-L (inert gas) and PBF-EB (high vacuum) [384,388].

The phases formed are affected by the thermodynamics and kinetics of phase transformations, which in turn are affected by the alloy’s composition. In the study by Kong et al. [404], Laves precipitates were not detected in the as-built microstructure when the Nb content was below 2 wt%, and they were detected at higher Nb contents. However, much of the work to date on controlling alloy compositions is focused not on controlling phases but instead on controlling defects, especially cracking, as discussed in the next section.

The majority of work on controlling phases is thermally based. It has been applied to both precipitates formed during solidification and those formed via solid-state phase transformations [391,410]. The size of Laves particles, closely correlated to that of the $\gamma$ dendrites, is largely affected by the cooling rate. For example, for the DED-L of IN718, Xiao et al. [391] observed long chain-like Laves particles along the boundaries of coarse columnar dendrites in a continuous-wave laser. When a pulsed laser was used and the resultant cooling rate was high, fine, disperse Laves particles formed along the boundaries of refined dendrites.

The fast-traveling heat source used in AM results in a cooling rate that is generally too fast for solid-state transformations to take place. However, the high preheat inherent to PBF-EB and the heat build-up in DED can expose the material locally to evaluated temperatures over an extended time. Upon slow cooling from the evaluated temperatures, strengthening precipitates $\gamma'$ and $\gamma''$ can form in the as-built microstructure. For example, cuboidal $\gamma'$ with a volume fraction of 59% was observed in the as-built microstructure of Rene 142 printed by PBF-EB [374]. Additionally, Sames et al. [389] intentionally heated the top surface of a completed build by a scanning electron beam and achieved in-situ solution treatment and aging of IN718.

5.1.3. Control of common defects

Common defects in additively manufactured nickel alloys include porosity due to lack of fusion or keyhole instability, spattering due to ejection of liquid metal droplets or powder particles, surface roughness caused by stair-step effect, instabilities of the molten pool, or partially melted powder particles attached to the surface, and various cracking issues [3,4]. Porosity defects are commonly mitigated by printing process optimization. Moreover, defects such as porosity, spattering, and surface roughness can be mitigated by additional post-fabrication processing such as hot isostatic pressing (HIP) or machining. The following discussion is thus focused on the control and mitigation of cracking, which is the most detrimental defect hindering the qualification of many high-temperature nickel superalloys for AM.

5.1.3.1. Cracking. Similar to welding, fusion-based additive manufacturing subjects a nickel alloy, especially that containing a high amount of $\gamma'$ forming elements (e.g., Al and Ti) to a wide range of cracking issues including solidification cracking, liquation cracking, ductility dip cracking, and strain age cracking [3,4]. Compared to welding, the susceptibility to cracking for AM is generally lowered due to the fine microstructures common in PBF and the high preheat inherent to PBF-EB. However, obtaining crack-free parts remains difficult for unweldable, precipitation strengthened nickel alloys, and cracking remains an important issue for nickel alloys.

Mechanisms for crack formation are complex but they typically involve the thermally-induced tensile stress and the material’s resistance to cracking at high temperatures [359]. The approaches to control and mitigate cracks tackle one or both of these factors, and they can be divided into two categories: metallurgical based, and processing based.

Designing alloy compositions that can produce crack-free parts by AM lies at the heart of the metallurgical-based approach. Tang et al. [410] performed a comprehensive alloys-by-design study where the effect of alloying composition on various cracking susceptibilities was computed computationally. For example, the susceptibility to solidification cracking was analyzed based on the freezing temperature range and solidification cracking index, and the susceptibility to solid-state cracking was analyzed based on the temperature and extent of $\gamma'$ precipitation. Their analyses led to the development of a new experimental alloy that contained 1.29 wt% Al and 2.22 wt% Ti. The alloy printed by PBF-L was free of cracks, and the heat-treated material had a low-temperature strength comparable to but somewhat lower creep performance than CM247LC. Jena et al. [411] studied LW 4275 nickel superalloy which contained 5.1 wt% Al but no Ti. The alloy printed by PBF-L was also free of cracks. After post-fabrication heat treatment, $\gamma'$ with volume fraction of 48% was formed. Compared to conventional alloys such as IN738 and Rene 80, the printed LW 4275 had somewhat inferior creep properties but superior ultimate tensile strength and elongation.

For nickel alloys that are considered weldable but can still suffer from cracking, tighter control of the alloy composition can reduce the cracking issue in AM. For example, Harrison et al. [412] controlled the composition of a modified Hastelloy X in such a way that the concentration of solid solution strengthening elements (e.g., W) was slightly increased and that of the tramp elements (e.g., Mn) was slightly decreased when compared to a standard Hastelloy X. The modified alloy, which composition was still within the pertinent industry specification, displayed a 65% reduction in solid-state crack density when compared to the standard alloy.

Instead of modifying the feedstock composition as in [67,410–414], Zhang et al. [415] modified the local composition in-situ during the DED-L of IN738. An IN718 layer was deposited every 2 layers of IN738 to create a layered, composite material that was free of cracks, as shown in Figure 5.4(a). Since the printing of IN718 did not interrupt the epitaxial growth of grains, the mechanisms for crack mitigation were attributed to the disruption of $\gamma'$ precipitates as well as the thermal stress on IN738 alleviated by the softer IN718.

The addition of inoculants represents another group microstructure-based approach to control solidification cracking [416]. As discussed earlier, Han et al. [399] studied the addition of TiC particles to Hastelloy X for PBF-L. The addition of 3 wt% TiC
nanoparticles [399] refined the grains and thus increased grain boundaries, which in turn mitigated intergranular microcracks, as shown in Figure 5.4(b). The addition of 2 wt% TiB\textsubscript{2} particles to Hastelloy X was also found to refine the grains and mitigate the cracks in PBF-L [417].

Controlling scanning strategies and processing parameters is commonly used for mitigating cracking issues. Catchpole-Smith et al. [418] studied the effect of scanning strategies on cracking in CM247LC printed by PBF-L. The cracks were identified as solidification and liquidation cracks. It was found that the fractal scanning strategy where the laser traveled in a tortuous path based on Hilbert or Peano-Gosper area filling curve reduced the crack length density when compared to the conventional island scanning strategy. No significant difference in microstructure was observed between the two scanning strategies, and thus the reduction in cracking was attributed to the prevention of stress build-up when the fractal scanning strategy was used. It is noted that cracking was not eliminated in their study. Kontis et al. [419] used a higher scanning speed and a reduced hatch spacing to obtain a fine-grained microstructure in an unweldable nickel alloy containing 5.30 wt% of Ti and 8.70 wt% of Al printed by PBF-EB. They identified that liquidation cracking was caused by micro-segregation of B, Cr, and Mo to high-angle grain boundaries (HAGBs). The cracks were mitigated for a fine-grained equiaxed or a columnar microstructure with a grain width smaller than 100 μm. It is expected that the high preheat of 1050 °C (1323 K) used in their study helped with the mitigation of cracks. The importance of build temperature on crack formation was studied in PBF-EB of CMSX-4 by Ramsperger et al. [363]. It was found that the pyramid-shaped samples contained cracks at the lower build temperature of 940 °C (1213 K) and did not contain cracks at the higher build temperature of 1040 °C (1313 K).

The application of external heating is another processing-based approach. Seidel et al. [420] used induction heating to preheat the substrate’s top surface temperature to 900 °C (1173 K) for DED-L of Mar-M247 and CM247LC alloys. Such high preheat decreased the temperature gradient between the melt pool and the substrate and consequently the thermally induced tensile stress. As a result, solidification and liquidation cracking was significantly reduced, as shown in Figure 5.4(c). They further demonstrated the use of high preheats for printing a miniature turbine blade made of CM247LC. The preheat temperature was increased to 1100 °C (1373 K). Lee et al. [416] also used a high preheat of 1025 °C (1298 K) for PBF-EB of Mar-M247. Asymmetric cracking was observed in cylindrical parts built at tilting angles from 30 to 50°. The microstructural factor for cracking was ruled out, and the thermally induced tensile stress was identified as the cause of cracking. The studies by Seidel et al. [420] and Lee et al. [416] indicate that the use of high preheat is necessary but may not be sufficient to fully mitigate cracking when printing un-weldable nickel alloys. The thermally induced stress still needs to be managed.

Kalentics et al. [417] applied laser shock peening after printing every n-th layer, where n = 3, 10, or 20, during PBF-L of CM247LC. Compared to untreated alloy, a significant reduction in bulk crack density by up to 95% was obtained using laser shock peening. It was postulated that the crack reduction was caused by the introduction of a compressive stress field near the laser shock-peened surface. Vertical cracks formed during printing would be closed by such a compressive stress field. Upon deposition of additional layers, the closed cracks were reheated and diffusion caused the cracks to be healed.

In summary, the elimination of cracks remains a significant challenge for AM of unweldable nickel alloys. Designing new alloy compositions with sound printability is most desirable. While a tremendous stride has been made in the alloy design considering various cracking susceptibilities, the published literature shows that the creep properties of new printable alloys are yet to match those of conventional high γ’ nickel alloys, e.g., CM247LC and IN738. The use of high preheat is essential to mitigate solidification or liquidation cracking although the thermally induced stress needs to be carefully managed to avoid cracking.

5.1.3.2. Lack of fusion, porosity, and composition change. Additively manufactured nickel alloy parts are susceptible to the lack of fusion voids and gas porosity both of which significantly degrade the mechanical properties of the parts [421–423]. Improper fusional

![Fig. 5.5.](image-url)
bonding among the neighboring tracks results in the lack of fusion voids. Moisture from the atmosphere and the gas entrapped inside the gas-atomized powders often cause gas porosity inside the component. Pores can also be generated from the gas bubble originating from a collapse of a keyhole. The shape and size of pores and voids can vary significantly. Fig. 5.5 shows the morphologies of keyhole pores and the lack of fusion voids during PBF-L of a nickel alloy IN713C [424]. Keyhole pores are spherical but elongated in shape and their size varies significantly. In contrast, the lack of fusion pores are often irregular in shape and often they are bigger than the gas pores. Pores are observed in optical micrographs of Inconel 718 samples produced by PBF-L with varying laser power and laser scan speed [425]. Keyhole pores are found at a very high laser power or slow scan rates. In contrast, at low power or high speed, the lack of fusion voids are formed due to insufficient melting. Therefore, optimum combinations of powers and speeds are necessary to print void-free parts. Printing parts using smaller hatch spacing can significantly reduce the lack of fusion in Inconel 718 parts made by PBF-L [425].

Nickel alloys generally consist of nickel, chromium, molybdenum, aluminum, iron, and some other elements in small quantities. These elements have very different vapor pressures. Therefore, they vaporize at different rates from the molten pool. This selective vaporization of different alloying elements results in a change in the part composition compared with the feedstock. For example, Fig. 5.6 shows that the composition of the constituting elements changes significantly during PBF-L of Inconel 718 [114]. Composition change can degrade the microstructure and corrosion resistance and may cause defects such as cracking. An optimum set of processing conditions need to be found to reduce composition change which is often done by using well-tested mechanistic models.

5.2. Single crystals of nickel alloys

In a single crystal (SX) part, the crystal lattice of the entire component is continuous with no grain boundaries [426]. The absence of defects related to the grain boundaries can provide the single crystal components with unique mechanical properties such as superior high temperature creep resistance [426]. That is why single crystal parts are used in high-temperature applications such as turbine blades in a jet engine [427]. Printing single crystals using additive manufacturing (AM) is a recent concept and is getting popularity because of its unique advantage of repairing cracks in expensive turbine blades with desired microstructure and properties. The literature on AM of SXs is growing and therefore it is necessary to include the fundamentals of printing SXs and their structure, properties, and performance in this review. This section describes the commonly used AM processes for the manufacturing of SX parts. In addition, theories for directional solidification to maintain single crystallinity are discussed. Furthermore, a comprehensive comparison of the mechanical properties of printed SXs and conventionally processed SXs is provided. Finally, control strategies for stray grain formation and defects in SX are reviewed.

5.2.1. Theories of printing single crystals

Deposition and repair of single crystals require close control of process variables to achieve solidification growth rates and temperature gradients. The main task is to avoid equiaxed grain formation by controlling solidification parameters, such as appropriate temperature gradient (G) and solidification growth rate (R). In addition, providing a high power density ensures sufficient depth of melting to have epitaxial growth with the underlying crystal. In addition to thermal control of G and R values, SX solidification also requires appropriate seeding. In such solidification, a solid grain is nucleated from the liquid onto a substrate in contact with the liquid. The substrate (or the seed) provides direction to the new grain growth and if appropriate thermal conditions are met, this grain can become an SX grain. A noteworthy point is this mode of solidification requires the partial or complete melt back of the substrate which provides seeding for the grain growth. Hence, the substrate must be an SX one if SX solidification is required. However, having an SX substrate does not guarantee SX solidification if the thermal conditions are not adequate and appropriate. This requirement was later

Fig. 5.6. Change in concentration of elements for (a) varying scan speed, (b) varying power during PBF-L of Inconel 718. The figure is made using data reported in [114].
proved to be wrong by Gotterbarm et al. [428] who successfully deposited SX Inconel® on EQ Inconel® via a novel scan strategy during E-PBF.

A good starting point is to use a well-tested model [185,429–431] of heat transfer and fluid flow that can provide solidification parameters from process variables so that maps of solidification growth rates and temperature gradients can be constructed from process variables. Plots of solidification growth rates versus temperature gradients can then be used to avoid equiaxed grains and achieve deposition of repair of single crystals. In addition, sufficient depth of the fusion zone can ensure epitaxy with the previously deposited layer.

5.2.2. AM processes for printing single crystals

Both powder bed fusion and directed energy deposition processes [2,3,8] are used to print single crystal alloy parts. For example, nickel alloy CMSX-4 is printed using PBF-L [432–434], DED-L [435], and PBF-EB to make single crystal parts [436–440]. DED-L is also used to make single crystal parts [441] of another nickel alloy Rene N5. Table 5.2 summarizes the recent applications of different AM processes to print single crystal parts. The most important criteria to print a single crystal is to maintain a particular temperature gradient [29,442,443] and solidification growth rate [29,442,443] throughout the process to facilitate directional solidification [441]. Desired temperature gradient and solidification growth rate to grow single crystals are often achieved by preheating the powder bed [436–440] and using complex combinations of scanning patterns and scanning speeds [435,441].

5.2.3. Recent examples of printed single crystals of nickel alloys

Additively manufactured single crystals can be of different sizes. For example, Fig. 5.7 (a) shows a longitudinal section of a 75 mm long and 12 mm diameter CMSX-4 single crystal cylinder [440] fabricated using PBF-EB. The horizontal section of the SX cylinder as well as the EBSD mapping shown in Fig. 5.7 (b) also indicate the single crystallinity of the component. Additively manufactured single crystals can be grown from both single-crystalline as well as polycrystalline substrates of different shapes and sizes. SXs of nickel-base superalloys such as CMSX-4 and Rene are manufactured and repaired using AM [432–434]. Since most of the nickel base superalloys exhibit FCC structure, AM build direction [440] is commonly along (001). Several researchers have printed components with dendrites aligned along (001) with very small misorientation angle among them and termed them as single crystals [441]. In those cases, dendritic arm spacing is an important microstructural feature that controls the mechanical properties of the component [441]. In SXs of nickel alloys, secondary phases such as laves phase are often observed [441]. Recent examples of additively manufactured single crystals of nickel alloys along with their important features are summarized in Table 5.2.

5.2.4. Properties of printed vs conventionally processed SXs

Single crystal AM parts often show poor tensile strength due to a lack of grain boundary strengthening [440]. Often unwanted secondary phases form in additively manufactured SXs which also affect the tensile properties of the part [440]. Due to the absence of grain boundaries, tensile properties of additively manufactured SXs are generally isotropic unlike common AM parts [440].

There are two main reasons why additively manufactured SXs are better than those processed conventionally. First, cracks in expensive, single-crystal turbine blades can be repaired by AM by depositing material inside the crack where the deposited material has the same microstructure as the original component [432,433]. Second, printed single crystal parts are often found to have high

<table>
<thead>
<tr>
<th>AM process</th>
<th>Alloys</th>
<th>Descriptions and features</th>
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<tbody>
<tr>
<td>PBF-L CMSX-4</td>
<td>Rapid scanning of the laser beam (up to 2 m/s) and high-resolution raster scanning (20 to 200 μm hatch spacing) were used to achieve the temperature gradient of 10^8 to 10^9 K/m necessary for directional solidification.</td>
<td>[432,433]</td>
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<tr>
<td>PBF-L CMSX-4</td>
<td>A bi-directional raster scanning pattern combined with a rapid scanning in the order of one m/s was used to achieve directional solidification.</td>
<td>[434]</td>
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<td>DED-L Rene N5</td>
<td>Around 5 mm tall parts were deposited that exhibited stray grains near the top.</td>
<td>[435]</td>
<td></td>
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<tr>
<td>PBF-L Rene</td>
<td>A raster scanning pattern by a very focused beam was implemented to achieve the directional solidification.</td>
<td>[444]</td>
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<tr>
<td>PBF-EB CMSX-4</td>
<td>A preheating temperature of 1270 K combined with a unique bi-directional scanning strategy where the scanning direction is rotated by 90° between two consecutive layers was used to achieve the directional solidification.</td>
<td>[436]</td>
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<tr>
<td>PBF-EB CMSX-4</td>
<td>The powder bed was preheated to 1273 K. In addition, a ‘cross snake hatch strategy’ was used where the scanning direction is rotated by 90° between two consecutive layers. Both helped to obtain the directional solidification. Processed parts were cylindrical with 12 mm in diameter and 78 mm in height. However, the parts suffered from porosities.</td>
<td>[437]</td>
<td></td>
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<tr>
<td>PBF-EB CMSX-4</td>
<td>A preheating temperature of 1273 K and a special scanning strategy were used to achieve directional solidification.</td>
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<tr>
<td>PBF-EB CMSX-4</td>
<td>The bed was preheated to 1223 K to achieve directional solidification. However, the details of the scanning pattern used were not provided. Parts are 5 × 5 × 5 mm^3 cubes. However, the parts suffered from γ’ precipitates.</td>
<td>[439]</td>
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<tr>
<td>PBF-EB CMSX-4</td>
<td>A preheating temperature of 1273 K and a ‘cross snake hatch strategy’ were used where the scanning direction is rotated by 90° between two consecutive layers. Both helped to obtain the directional solidification.</td>
<td>[440]</td>
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<tr>
<td>DED-L Rene N5</td>
<td>SX cylinders of 75 mm in length and 12 mm in diameter were produced. Processing conditions were optimized to achieve single crystallinity by trial and error. Further details were not provided.</td>
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temperature creep properties (Fig. 5.8) comparable to those in conventionally processed components [436].

AM is used to repair SX turbine blades that require superior high temperature creep properties [436,444]. It depends on consistency in the microstructure of the repaired part with the original component. However, the formation of stray grains and unwanted secondary phases often significantly degrade the creep properties of the repaired components [435,445]. With an appropriate post-process heat treatment, additively manufactured SXs can achieve superior fatigue life compared to conventionally processed SX components [440]. However, often internal cracks in the repaired part can be a source of stress concentration and significantly reduce

Fig. 5.7. A single crystal part of a nickel alloy, CMSX-4 made by PBF-EB. (a) Vertical cross-section, and (b) horizontal cross-section and EBSD mapping [440]. Y and Z directions are along the radial and height directions, respectively.

Fig. 5.8. A single crystal CMSX-4 part made by PBF-EB shows comparable high temperature creep properties to conventionally processed single crystal [440].
5.2.5. Prevention of stray grain formation and defects

Printing of single crystal parts is often hindered by the formation of stray grains [435,445] primarily near the top edge of the deposit (Fig. 5.9). Stray grains may form due to heterogeneous nucleation originating from free powder particles near the top surface (Fig. 5.10) of the deposit [435,445]. High convective and radiative heat losses from the top surface that disrupts directional solidification may also form stray grains [435,445–447]. For example, Liang et al. [435] showed depositions of an SX that contains stray grains near the top of the deposited part, as shown in Fig. 5.9. Prediction of temperature gradient and solidification growth rate can be effective to estimate conditions for stray grain formation [446,447]. Post-process heat treatments or machining of the regions with stray grains are often necessary to achieve a complete single crystal component. In addition, cracking [445] due to solidification shrinkage [448] is another major issue in AM of single crystal parts. Furthermore, it is also challenging to predict appropriate preheat temperature, heat input, and scanning strategy to achieve directional solidification to grow single crystals [445].

Printing of SX is a recent concept and the literature on this topic is growing. Currently, only nickel and titanium alloys can be printed to fabricate single crystals. Wider acceptance of AM for printing SXs also depends on the solution to the major problems associated with the process. The use of well-tested mechanistic models and machine learning can be an option in the future to help alleviate these problems and make the printing of single crystals for various alloys economically viable.

6. Control of grain structure, phases, and defects in titanium alloys

Additive manufacturing allows cost-effective fabrication of Ti-alloy parts because of a low buy-to-fly ratio compared to traditional manufacturing processes. In addition, the mechanical properties of Ti alloys can be modified extensively by alloying, heat-treating, and deformation processing. They are immune to corrosive attacks by many acids and chlorides and are non-toxic and biocompatible. The combination of lightweight, sound mechanical properties, corrosion resistance, and high-temperature endurance makes Ti alloys suitable for aerospace, biomedical, and other applications. However, the printed titanium alloy parts exhibit grain structures and phases that are very different from their wrought counterparts produced with conventional manufacturing methods. In addition, additively manufactured Ti alloy parts suffer from common defects. Therefore, an understanding of how to control the grain structure, phases, and defects is essential. This section of the review focuses on control strategies of grain structure, phases, and defects (Fig. 6.1) during AM of titanium alloys. Table 6.1 provides selected examples of controlling grain structure, phases, and defects in additively manufactured titanium alloy parts. Given their widespread use, at first, we focus on \( \alpha + \beta \) alloys, in particular the Ti-6Al-4 V alloy. Then an assessment of controlling grain structure, phases, and defects in metastable \( \beta \) alloys is discussed owing to their importance in aerospace and biomedical applications.

6.1. Control of grain structure, phases, and defects in \( \alpha + \beta \) alloys

6.1.1. Strategies to control grain structure

In titanium alloys, large columnar \( \beta \) grains (BCC) form after solidification. During cooling, below a critical \( \beta \)-transus temperature, \( \alpha \) grains (HCP) form within the prior \( \beta \) grains structure [449]. AM of Ti alloys involves the formation of large columnar prior \( \beta \) grains.
which parameter is most useful, although \( Q \) has been found to relate to the final grain size via a relationship of the form \\

\[
\text{amount of supercooling at steady-state growth.}
\]

Note that both \( Q \) and \( P \) increase with increasing solute content. Debate continues over \\

supercooling parameter and is expressed as \\

6.1.1.2. Grain refinement by controlling undercooling. 

Heat input because it may result in the formation of defects. 

is the alloy composition [455]. The second parameter \( Q \) is referred to as the growth restriction factor and is given by: \\

\[
P = \frac{m C_o (k - 1)}{k}
\]

Overall, the structures coarsened with the increasing height of the wall. The width of the columnar grains increased with 

greater distance from the substrate as did the layer height in both high and low power builds due to heat accumulation. 

The width of the entire HAZ at the substrate/deposit interface was found to be wider with higher laser power (Fig. 6.2). 

It was reported that the high power reduced the cooling rate and resulted in a coarser microstructure. The formation of columnar prior \( \beta \) grains was compared [450] 

for DED-L and DED-GMA of wall builds of Ti-6Al-4 V about 250 mm long and 7.5 mm wide. Columnar grains were observed extending 

over many layers in both processes due to continued epitaxial growth from prior layers. However, there was a clear difference in the 

width of the columnar grains with much larger grains seen in the DED-GMA samples due to the much higher heat input compared to 

DED-L. Waryoba et al. [454] compared the solidification structures of Ti-6Al-4 V parts made using laser and electron beam-assisted AM 

processes. The higher energy density of the electron beam process exhibited slower cooling and resulted in coarse \( \alpha \) basketweave 

structures with large prior \( \beta \) grain size with a columnar morphology. In contrast, the lower energy density of the laser process resulted in 

a fine \( \alpha \) basketweave structure within transformed columnar grains. However, the prior \( \beta \) grain size of the columnar structure was 

finer. Thus, the grain structure can be effectively controlled by adjusting the heat input. However, care should be taken in adjusting the 

heat input because it may result in the formation of defects.

6.1.1.1. Control of solidification morphology. 
The solidification morphology (columnar or equiaxed) is affected by the ratio of the 

temperature gradient at the solid/liquid interface (G) and the solidification growth rate (R). At low values of \( G/R \), equiaxed dendritic 

grains may nucleate in the constitutionally supercooled region just ahead of the solid/liquid interface (see section 2). The scale of the 

microstructure is indicated by the product GR which is known as the cooling rate. Therefore, control of solidification structures can be 

done by adjusting \( G \) and \( R \). During AM, \( G \) and \( R \) are affected by the heat input. In AM, heat input per unit length increases with 

increasing power and decreasing scanning speed.

The effects of heat inputs in controlling the formation of columnar grains have been demonstrated in several studies [450–453]. 

Zhai et al. [451] conducted a systematic investigation of the microstructure of Ti-6Al-4 V wall builds \((2\,\text{in} \times \frac{1}{2}\,\text{in} \times \frac{1}{2}\,\text{in})\) using two laser powers. Overall, the structures coarsened 

with the increasing height of the wall. The width of the columnar grains increased with 

greater distance from the substrate as did the layer height in both high and low power builds due to heat accumulation. The width of the entire HAZ at the substrate/deposit interface was found to be wider with higher laser power (Fig. 6.2). It was reported that the high power reduced the cooling rate and resulted in a coarser microstructure. The formation of columnar prior \( \beta \) grains was compared [450] 

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finer. Thus, the grain structure can be effectively controlled by adjusting the heat input. However, care should be taken in adjusting the 

heat input because it may result in the formation of defects.

6.1.1.2. Grain refinement by controlling undercooling. 
The control of grain refinement is based on two parameters: \( P \) and \( Q \). \( P \) is a 

supercooling parameter and is expressed as 

\( P = \frac{m C_o (k - 1)}{k} \) where \( k \) is the partition coefficient, \( m \) is the slope of the liquidus, and \( C_o \) 

is the alloy composition [455]. The second parameter \( Q \) is referred to as the growth restriction factor and is given by: 

\( Q = m C_o (k - 1) \). 

The parameters \( P \) and \( Q \) are related by: 

\( P = \frac{Q}{k} \). 

\( Q \) can be interpreted as the initial rate of development of constitutional supercooling (CS) concerning fraction solid or 

\( Q = \left( \frac{d\Delta T_s}{df_s} \right)_{f_s=0} \) where \( f_s \) is the fraction of solid. Also, from the plot, it is apparent that \( P \) is the 

amount of supercooling at steady-state growth. Note that both \( Q \) and \( P \) increase with increasing solute content. Debate continues over 

which parameter is most useful, although \( Q \) has been found to relate to the final grain size via a relationship of the form 

\( d_{\text{grain size}} = a + \frac{b}{Q} \) where \( a \) and \( b \) are constants.

The theories described above were extended by St. John and coworkers [456–458] to include other key factors to develop the 

Interdependence Theory. The theory assumes that a series of successive nucleation events must take place continuously in front of the 

advancing solid/liquid (s/l) interface to allow the uniform formation of equiaxed grains. Briefly, the theory holds that the final grain 

size is determined by three factors: (i) the distance that a previously nucleated grain must grow to establish sufficient constitutional 

supercooling (CS) ahead of an s/l interface to enable the nucleation of the next grain; (ii) the distance from this s/l interface to the point 

that extend several layers or passes. This configuration results in anisotropic mechanical properties and is therefore undesirable. 

In addition, the mechanical properties of the Ti alloy parts are also affected by the shape and size of the \( \alpha \) grains. Several attempts have 

been made to break the long columnar prior \( \beta \) grains into smaller equiaxed grains and to control the shape and size of \( \alpha \) grains to 

improve the mechanical properties of parts. These methods are reviewed below.
where this critical amount of CS has been generated; and (iii) the additional distance to the nearest most potent nucleant particle. A distribution of nucleant particle sizes is considered, with the potency of a particle to promote nucleation of a new grain considered to be greater as the particle radius increases.

The Fig. 6.3 (a) illustrates one of the key points of the theory [458]. A new grain has nucleated successfully at the left and is growing radially. As it grows and rejects solute ahead of the s/l interface, a CS region is set up as shown. Here, $\Delta T_{s}$, $S_d$ and $X_{sd}$ represent the
undercooling required for nucleation, distribution of particle sizes, and average interparticle spacing, respectively. The theory assumes that nucleation occurs on the most potent particles. Without describing all the mathematical details, the $\Delta T_n$ versus $S_d$ curve that describes the potency and distribution of particle sizes [457] is shown in Fig. 6.3 (b). The key point that underpins the utility of the theory is that the location of the next nucleation event can be predicted as the intersection of the undercooling required for nucleation, $\Delta T_n$ versus $S_d$ curve with the actual local temperature in the melt pool ($T_m$), as shown in Fig. 6.3 (b) [457]. The location of the $\Delta T_n$ versus $S_d$ curve will shift to the left as the amount of solute is increased. The curve will also evidently shift to the left for larger particles. Using this approach, the average grain size can be estimated as the distance from the center of the already growing grain and the position of the new nucleation event. For the microstructure to be comprised completely of equiaxed grains, a wave of repeated nucleation must occur as the solid/liquid interface moves with each nucleation event triggering a new constitutionally supercooled region to allow replication and continuation [459].

### Table 6.1
Selected examples of controlling grain structure, phases, and defects in additively manufactured titanium alloy parts.

<table>
<thead>
<tr>
<th>Objective</th>
<th>Alloy</th>
<th>AM process</th>
<th>Description of control strategy</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control of grain structure</td>
<td>Ti-6Al-4 V</td>
<td>DED-L</td>
<td>Low laser power increased the cooling rate and reduced the size of columnar $\beta$ grains</td>
<td>[451]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>DED-GMA</td>
<td>Additions of up to 0.13 wt% B eliminated resulted fine equiaxed $\alpha$ grains and thinner</td>
<td>[462,463]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>$\beta$ stabilizing elements V and Fe refined columnar $\beta$ grains</td>
<td>[464]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>$\beta$ stabilizing elements V and Fe refined columnar $\beta$ grains</td>
<td>[464]</td>
</tr>
<tr>
<td>Control of phases</td>
<td>Ti-Cu (up to</td>
<td>DED-L</td>
<td>This alloy was designed to have a high constitutional supercooling to mitigate the formation of</td>
<td>[467]</td>
</tr>
<tr>
<td></td>
<td>8.5 wt%)</td>
<td></td>
<td>columnar grains</td>
<td></td>
</tr>
<tr>
<td>Control of defects</td>
<td>Ti-6Al-4 V</td>
<td>DED-GMA</td>
<td>Post-process heat treatment refined $\alpha$ grains</td>
<td>[468]</td>
</tr>
<tr>
<td></td>
<td>Ti-5553 alloy</td>
<td>PBF-L</td>
<td>Post-process heat treatment resulted in precipitation of $\alpha$ phase that improved mechanical</td>
<td>[490]</td>
</tr>
<tr>
<td></td>
<td>Ti-5553 alloy</td>
<td>PBF-L</td>
<td>Low heat input produced single-phase $\beta$ microstructures with small amounts of $\alpha$ phase</td>
<td>[498]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>Low energy density resulted in $\alpha$-martensitic or $\alpha$/$\alpha'$ microstructures that</td>
<td>[469]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>DED-L</td>
<td>Low laser power resulted in rapid cooling and produced martensitic $\alpha'$ microstructures</td>
<td>[451]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>DED-PA</td>
<td>Low laser power resulted in martensitic $\alpha'$ microstructures</td>
<td>[470]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>DED-L</td>
<td>Post-process vacuum annealing heat treatment produced $\alpha + \beta$ microstructures that</td>
<td>[451]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>DED-PA</td>
<td>$\beta$ stabilizing elements V and Fe refined columnar $\beta$ grains</td>
<td>[467]</td>
</tr>
<tr>
<td>Control of defects</td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>Low hatch spacing ensured overlaps among neighboring tracks and reduced the lack of fusion</td>
<td>[119,481]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>High laser power increased the pool dimensions, improved fusional bonding, and reduced the</td>
<td>[480]</td>
</tr>
<tr>
<td></td>
<td>Ti-5553 alloy</td>
<td>PBF-L</td>
<td>High heat input resulted in larger pool and better fusional bonding, and reduced the lack of</td>
<td>[498]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>High heat input resulted in larger pool and better fusional bonding, and reduced the lack of</td>
<td>[498]</td>
</tr>
<tr>
<td>Control of defects</td>
<td>Ti-6Al-4 V</td>
<td>PBF-L</td>
<td>Post-process hot isostatic pressing reduced the number of voids</td>
<td>[482]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4 V</td>
<td>PBF-EB</td>
<td>Change in aluminum composition due to selective vaporization was reduced by adjusting the heat</td>
<td>[485]</td>
</tr>
</tbody>
</table>

### 6.1.1.3. Addition of boron for grain refinement
The addition of boron for grain refinement in titanium alloys was widely practiced in casting and fusion welding. For example, it was found that additions of B up to 0.4% significantly refined the microstructure of cast Ti alloys [460] which improved the tensile strength and toughness. In a different study, it was found that additions up to ~0.1 wt% B provided a large decrease in grain size in cast Ti-6Al-4 V and Ti-6Al-2Sn-4Zr-2Mo (Ti-6242S) alloys [461]. The grain size ranged from ~1700 μm for no B additions to ~200 μm for 0.1% B. The grain refinement occurs due to a change in the undercooling behavior because of the boron addition. In AM, grain refinement due to boron addition was reported for DED-GMA of Ti-6Al-4 V [462,463]. Additions of B (up to 0.13 wt%) eliminated grain boundary-$\alpha$ and colony-$\alpha$ and generated a uniform microstructure of fine equiaxed-$\alpha$-grains in both as-deposited and heat-treated conditions. Prior-$\beta$ grains remained columnar with B additions but become thinner due to the larger solidification temperature range and growth restricting effect of B. Boron additions were claimed to generate narrower columnar grains due to lateral solute rejection during epitaxial growth from previous layers [462,463]. However, the amount of boron needed to refine the grains are currently selected by trial-and-error and requires a quantitative formalism based on scientific principles.

### 6.1.1.4. Additions of $\beta$ stabilizing element for grain refinement
The elements that stabilize $\beta$ are added to refine grains during AM of titanium alloys [25,453,464–466]. For example, additions of V and Fe for grain refinement during PBF-L of Ti-6Al-4 V have been reported [464]. The in-situ additions of $\beta$-stabilizing elements V and Fe resulted in an alloy with a composition close to the $\beta$ alloy, Ti-10 V-2Fe-3Al. Instead of $\alpha'$ microstructure expected during PBF-L of Ti-6Al-4 V, the additions of Fe and V yielded an $\alpha + \beta$ microstructure containing up to ~63% $\beta$. Heat-treatment below the $\beta$ transus permitted precipitation of the nanoscale $\alpha$ phase in the $\beta$ matrix and produced high strength and good ductility [464]. W, Nb, and Mo were added by Tedman-Jones et al. [466] for grain refinement.
These elements have higher melting points than Ti and exhibit a bcc crystal structure like Ti at temperatures near their melting points. Small powders of these elements added to the Ti-6Al-4 V act as nucleating sites for grain refinement. A supercooled region formed around the W, Nb, or Mo particles due to their dissolution causing the particles to act as sites for nucleation and subsequent growth of fine grains (Fig. 6.4). Care should be taken to select an optimum initial particle size that will maximize the number of nucleation sites and promote grain refinement during solidification while not dissolving too quickly during AM [466].

6.1.1.5. Design of new alloys for controlling grain structure. Ti-Cu (up to 8.5%) alloy [467] was designed to have a high constitutional supercooling capacity because of the partitioning of Cu during solidification, which can mitigate the formation of columnar grains. The as-deposited Ti-Cu alloy specimens had a fully equiaxed fine-grained microstructure [467]. The cooling rate was slower and diffusional transformations dominated microstructural development. In these cases, a fine eutectoid lamellar structure (α + Ti2Cu) formed with some hyper-eutectoid primary Ti2Cu particles of larger size. Reheating above the eutectoid temperature (792 °C) during multilayer deposition removed the α′ phase formed initially and produced the very fine eutectoid lamellae. Samples of alloys containing up to 8.5% Cu could be produced, and the α phase was supersaturated (2.8% Cu vs 2.0% solubility limit from the phase diagram) indicating that further strengthening could be achieved with additional heat treatment. The alloys also displayed improved mechanical properties, comparable to wrought Ti-6Al-4 V alloys [467]. Cu is an inexpensive alloying element relative to many other elements used in Ti alloys, making these new alloys even more attractive. However, the density of Cu is almost twice that of Ti. Therefore, care should be taken to maintain the density of the alloy for critical applications where the part weight is a critical factor such as in aerospace industries.

6.1.1.6. Heat treatment for controlling grain structure. Heat treatments below the β-transus temperature (sub-transus) offer the potential for improved ductility while maintaining high strength. Wang et al. [468] produced Ti-6Al-4 V samples using the DED-GMA process and performed different sets of sub-transus heat treatments indicated by (a), (b), and (c) in Fig. 6.5. The figure describes the microstructural evolution for each heat treatment. The microstructure for this heat treatment was comprised of fine discontinuous αGB, αp, and dispersed αs where the subscripts for the α phase refer to the following: GB is grain boundary, p is primary, and s is secondary. In heat treatment (a), rapid cooling due to the water quenching formed α′ martensite. Relatively slower cooling [468] in the air formed αp. Dispersed secondary α phase was formed in heat treatments (b) and (c) which improved the strength and ductility. Two mechanisms of αp break-up during heat treatment were identified [468]. The mechanisms included termination migration involving chemical potential gradient-driven diffusion and boundary splitting or shearing across the lath. The solute concentration gradient within a groove undergoing migration was observed. Although post-process heat treatment can significantly improve the grain structure and mechanical properties, they add costs.
6.1.2. Phase control strategies

Pure titanium experiences an allotropic transformation from a body-centered cubic (bcc) phase (β phase) to a hexagonal close-packed (hcp) phase (α phase) on cooling at approximately 885 °C (β transus temperature) [449]. The β transus temperature of titanium alloys varies depending on the composition. For example, the β transus temperature for the Ti-6Al-4 V alloy is ~ 975 °C ± 25 °C depending on the amount of O and Fe impurities [449]. Alloy designations for Ti alloys are based on their equilibrium crystal structures at ambient temperature and broadly include α, α + β metastable β and stable β alloys depending on the balance of α stabilizers (Al, O, N and others) and β stabilizers (V, Cr, Nb and others). Beta (β) stabilizing alloy elements can be further classified as those that promote either isomorphous or eutectoid phase diagrams. Some alloy additions (ex. Sn, Zr) have little influence on the stability of either phase and are added for purposes of solid solution strengthening. Formation of an hcp α' phase by a martensitic reaction is also possible at faster cooling rates from the β phase field [449]. Moreover, an α'' phase with an orthorhombic structure can form in binary and higher-order systems containing Ti and β stabilizing transition metals (TM) at alloying levels greater than found for α' phases. At higher content of β stabilizing alloy additions, metastable β' and ω (omega) phases can also form at high cooling rates. Finally, secondary α (αS) may be found that are heated to the β phase field and then quickly cooled again before all α is dissolved. The αS phase typically

Fig. 6.3. (a) A new grain has nucleated successfully on left and is growing radially. As it grows and rejects solute ahead of the solid/liquid interface, a constitutional supercooling (CS) region [458] is set up as shown. the ΔTn versus Sd curve that describes the potency and distribution of particle sizes. Here, ΔTn and Sd represent the undercooling required for nucleation [457] and distribution of particle sizes, respectively. T_E and T_A indicate the equilibrium liquidus temperature and actual temperature, respectively. The suffix ‘nfz’ represents nucleation-free zone. (b) Growth of particles. Here, the suffix ‘min’ indicates the minimum value. We have redrawn this figure.
forms on the existing (or remaining) primary $\alpha$ phase \[449\]. The control strategies for phase formation during AM of titanium alloys are reviewed below.

6.1.2.1. Controlling heat input and substrate geometry. Heat input and its influence on cooling rates play a key role in controlling microstructural features during AM of titanium alloys. High energy density during PBF-EB exhibited slower cooling and resulted in an $\alpha + \beta$ microstructure in Ti-6Al-4 V parts \[469\]. In contrast, rapid cooling at relatively lower energy density during PBF-L resulted in $\alpha'$ martensitic or $\alpha/\alpha'$ microstructures \[469\]. In Ti-6Al-4 V parts made by DED-L, lower laser power resulted in rapid cooling and produced martensitic $\alpha'$ microstructures \[451\]. In contrast, coarse fully $\alpha + \beta$ lamellar structures were observed in high power deposits \[451\]. A similar observation was also made during the DED-PA of Ti-6Al-4 V \[470\]. Thus, the formation of $\alpha$ and $\beta$ phases in additively manufactured Ti alloy parts can be controlled by adjusting the heat input.

Thicker substrates conduct more heat than thinner substrates. Therefore, substrate dimensions can influence heat flow, impact the deposit geometry and cooling rates, and produce spatial variations in microstructures \[471\] and several attempts have been made to control the phase formation by adjusting the substrate geometry. For example, Lin et al. \[470\] used this approach to control the phase formation during DED-PA of Ti-6Al-4 V (Fig. 6.6). Rapid three-dimensional heat conduction through the substrate resulted in martensitic $\alpha'$ and fine $\alpha + \beta$ basketweave phases near the substrate. However, the $\alpha'$ disappeared and the phases coarsened as the built height increased. Therefore, the formation of martensitic $\alpha'$ or $\alpha + \beta$ basketweave phases were affected by the heat conduction through the substrate which can be controlled by adjusting the substrate geometry. Similar observations were also made by Zhai et al. \[451\] during the DED-L of Ti-6Al-4 V. For these cases, variations in cooling rates at different substrate thicknesses controlled the phases. Mechanistic models need to be developed to simulate the 3D heat transfer and predict the appropriate substrate thickness to achieve cooling rates that can provide the desired grain size and phases.

6.1.2.2. Control of thermal cycles. Additively manufactured parts experience repeated heating and cooling due to multiple thermal cycles during multi-layer deposition. The formation of phases in printed Ti alloy parts is affected by thermal cycles in three distinct temperature regimes \[470\] in the solid-state: (1) above the $\beta$-transus; (2) below the $\beta$-transus but high in the two-phase $\alpha + \beta$ phase field; and (3) a temperature too low for any transformations. After solidification and cooling into the two-phase $\alpha + \beta$ field, primary $\alpha$ forms within a $\beta$ matrix. However, this structure is erased, at least partially, as the $\alpha$ partly dissolves during the next heating cycle. The extent of dissolution depends on the time and temperature. Microstructural changes cease when peak temperatures in the thermal cycles become too low for diffusional transformation. Often rapid cooling forms $\alpha'$ martensite, when thermal cycle minima fall below the Martensite start temperature (Ms) for the alloy \[470\]. The formation of these phases is affected by the multiple thermal cycles and thus can be controlled by adjusting the processing conditions \[472,473\]. For example, Fig. 6.7 shows the spatial variations in phase formation depending on the local thermal cycles during DED-GMA of Ti-6Al-7Nb alloy \[472\]. A banded microstructure was found below the $\beta$-transus temperature. The low-temperature region occurred two or three layers below the last pass due to the high heat input of the DED-GMA process and was not apparent in the last few passes. The lighter etching band resulted from local enrichment of Nb in the matrix when $\alpha_0$ formed and was not homogenized during later heating due to its lower diffusivity. Thermal cycles can be controlled by adjusting layer thickness, heat input, scanning patterns, and inter-pass dwell time to control the phase formation. However, care should be taken because adjustment of these process variables may also result in other issues such as the formation of defects.
6.1.2.3. Heat treatment to control the phases. Several attempts have been made to control the phases in printed Ti-alloy parts by using post-process heat treatments. For example, the DED samples of Ti-6Al-4 V were subjected to a vacuum annealing heat treatment (760 °C for 1 h followed by air cooling). The annealing process decomposed the martensitic α’ phase present in the as-deposited samples and resulted in a fine α + β microstructure. Zou et al. [474,475] showed that the heat treatment of PBF-L samples of Ti-6Al-4 V significantly changed the microstructure from that in the as-deposited parts (Fig. 6.8). The refinement of the lath structure occurred due to epitaxial recrystallization from α’/α interfaces in the α’ substructure that contained residual β phase. The EBSD images provided evidence of the early stages of nucleation and growth of new recrystallized β with high angle boundaries. The authors also indicate that the high dislocation density in the α’ martensite provided the driving force for the nucleation of new variants. Grain boundary α was also observed in all the specimens due to slow cooling after the heat treatment. From the discussion above, it is evident that the post-process heat treatment can be used to control the phases in the additively manufactured Ti alloy parts. However, the challenge remains in selecting an appropriate combination of heat treatment time and temperature. In addition, post-process heat treatment adds an extra cost that is often not desirable.

6.1.3. Control of common defects

Ti alloys are very sensitive to the pickup of impurity elements such as C, N, O, and H during processing which can cause severe embrittlement issues. In addition to embrittlement from impurities, the pickup of gaseous impurities during AM can also lead to porosity problems due to lower solubility in the solid. The extremely strong chemical affinity of the Ti alloy for O, N, C, and H often mandates the use of vacuum or nearly complete inert environments during fusion-based AM processes. In addition, additively manufactured titanium alloy parts are susceptible to other defects such as lack of fusion, porosity, and composition change. This section reviews the controlling strategies for these defects.
6.1.3.1 Reducing impurities by gas shielding effects. Ti alloys are very sensitive to the pickup of C, N, O, and H from the atmosphere. Inadvertent additions of these elements not only lead to porosity but embrittlement. Therefore, measures must be undertaken to shield the melt pool from contamination either by vacuum or proper inert gas shielding. Powder feedstocks, with their much greater surface-to-volume ratio relative to wire feedstocks, are expected to contain significantly greater amounts of O in terms of their surface oxide content. Moreover, they will typically have extensive amounts of physically or chemically adsorbed moisture depending on the local humidity levels. Carroll et al. [452] carried out DED-L of Ti-6Al-4 V using powder feedstocks in an argon chamber. They observed a pickup of 0.0124 wt% O but no extensive gas-derived porosity or embrittlement.

Bermingham et al. [476] performed experiments with DED-GMA of Ti-6Al-4 V to study the effects of absorbed oxygen. If no shielding was used, a thick brown oxide was formed. In those cases, the samples were allowed to cool to ambient temperature after each pass, and the oxide layer was removed using glass bead blasting before producing the next pass. This process can avoid the accumulation of oxygen and decrease embrittlement but reduce productivity. If no inter-pass glass bead blasting was used, the surface oxides appeared to be dissolved uniformly into the next pass. Therefore, it is recommended that an inert shielding gas should be used during AM of Ti alloys to reduce the impurities and the resultant embrittlement and porosity.

6.1.3.2 Controlling the lack of fusion and porosity. The low thermal diffusivity of titanium alloys is of particular interest relative to heat flow during AM and subsequent effects on defect evolution due to cooling rates. Titanium alloys are not susceptible to solidification or liquation cracking during AM. Moreover, Ti alloys are much less reflective to infrared laser beams relative to Al alloys, and coupling or back reflection issues during laser-based AM processes are not typically concerning. However, lack of fusion and porosity...
Improper fusional bonding among the neighboring tracks results in the lack of fusion voids that are irregular in shape (Fig. 6.9 (a)). Moisture from the atmosphere and the gas entrapped inside the gas-atomized powders often cause gas porosity inside the component. Gas pores are spherical (Fig. 6.9 (b)) and their size varies significantly. PBF-L is often performed in keyhole mode at a very high energy density. An unstable keyhole may collapse and the vapor bubble is entrapped inside the part to cause keyhole pores. These pores are elongated in shape (Fig. 6.9 (c)). All these three types of voids or pores significantly degrade the mechanical properties of parts [477].

Lack of fusion is affected by the extent of overlap between two consecutive tracks. The extent of overlap between tracks can be controlled by adjusting the molten pool size and the distance between two neighboring tracks. Lack of fusion defects are found to be

Fig. 6.7. Microstructure of a titanium alloy built (a). The microstructure near the top and bottom are shown in (b) and (c), respectively [472].

Fig. 6.8. Typical α-orientation maps of Ti-6Al-4 V in (a) as-built condition and (b) after heat treatment. Reconstructed β-orientation maps of Ti-6Al-4 V in (c) as-built condition and (d) after heat treatment [474,475].
dependent on layer thickness (L), hatch spacing (H), molten pool depth (D), and width (W). The lack of fusion voids can be prevented by achieving a proper combination of these four variables [124]. For example, at a constant laser power and scanning speed which indicate fixed values of pool width and depth, volume % of lack of fusion void in Ti-6Al-4 V parts made using PBF-L [119] increases with hatch spacing (Fig. 6.10 (a)). Lack of fusion defect in Ti-6Al-4 V parts made using PBF-L [481] was also found to increase with the hatch spacing. In contrast, the lack of fusion can be reduced by printing parts with thinner layers (Fig. 6.10 (b)). High laser power results in both wider and deeper pools that can reduce the lack of fusion as shown in Fig. 6.11 (a-c) for Ti-6Al-4 V components made using PBF-L [480]. The selection of appropriate combinations of processing conditions to avoid the lack of fusion is often performed by using mechanistic models of additive manufacturing.

Moisture or gas produced during the process can be entrapped inside the molten pool and after solidification, they remain inside the component as gas pores. Post-process hot isostatic pressing can reduce the number of voids [482]. For example, Fig. 6.11 (d-e) show that the pores in Ti-6Al-4 V parts made using PBF-L can be reduced using hot isostatic pressing [482] but adds an extra cost. Gas pores originating inside the molten pool can come out of the pool before solidification driven by the buoyancy and convective flow of molten metal. Therefore, the number of gas pores and their distributions are often affected by the convective flow of liquid metal inside the molten pool. Fig. 6.12 explains the molten pool dynamics and their effects on pore distribution [483] during DED-L of Ti6Al2Sn4Zr2Mo. Generally, the molten metal flows from the center (low surface tension) to the periphery (high surface tension) of the
pool. Time-resolved radiographs show the effect of flow patterns on the distribution of the pores. The distribution of the pores can be significantly different if the flow pattern is reversed. Often, the presence of oxygen which is a surface-active element can change the flow pattern and result in a different pore distribution. The number of gas pores that remains in the part and their distributions are affected by the pore size, viscosity of the molten liquid, convective flow, and solidification time. An in-depth quantitative formulation is needed to correlate these variables with the number of gas pores in the additively manufactured parts. The reduction of voids and pores in additively manufactured titanium alloy parts remains an important challenge to improving the mechanical properties of parts.

6.1.3.3. Minimizing composition change due to selective vaporization of alloying elements. Constituting elements of titanium alloys have very different vapor pressures at high temperatures. Therefore, they vaporize at different rates from the molten pool. This selective vaporization of different alloying elements results in a change in the composition of the part from the feedstock [484]. Composition change can degrade the microstructure and corrosion resistance. Experimental results [485] confirm the considerable loss of aluminum for the PBF-EB of Ti-6Al-4 V builds. The experimentally measured concentration of aluminum for various speeds and powers is shown in Fig. 6.13. In all cases, the concentration of aluminum in the build was significantly lower than that in the powder. As shown in the figure, both the energy of the beam and the scanning speed was varied, and for a given linear energy density, a higher scanning speed produced a higher aluminum composition change. Because faster scanning normally results in a shallower, longer molten pool with a larger surface area, the more pronounced composition change is consistent with the fact that a higher surface area to volume ratio will produce more vaporization per unit volume. A careful selection of process parameters, the spatial distribution of the energy of the heat source, and control of temperature are key to reducing the loss of volatile alloying elements.

6.2. Control of grain structure, phases, and defects in metastable \(\beta\) alloys

6.2.1. Metastable \(\beta\) alloys and their applications in additive manufacturing

Metastable \(\beta\) titanium alloys contain higher amounts of body-centered-cubic (bcc) forming elements such as V, Nb, Hf, and Ta which expand the \(\beta\)-bcc phase field and shift it to lower temperatures [486]. Additional alloying elements such as W, Fe, and Cr enhance eutectoid reactions of \(\beta\) titanium and ordered compounds, creating microstructures that are highly sensitive to thermal processing and heat-treating conditions. These alloys tend to have high strength-to-weight ratios with good corrosion resistance and are often used in aerospace applications but tend to be expensive, which limits their use to high-value-added components. There are
several alloys with different degrees of metastability depending on the relative amounts of alloying elements. The β stabilizing effectiveness of a given alloy can be approximated by a molybdenum equivalent, where each alloying element is assigned a multiplier for its β stabilizing ability relative to molybdenum [486]. Metastable titanium alloys have Mo-equivalent values between

Fig. 6.12. Molten pool dynamics and its effects on pore distribution during DED-L of Ti6Al2Sn4Zr2Mo under (a) radially outward fluid flow and b) radially inward flow. Time-resolved radiographs showing pore behavior in (b) to (d) for the condition of (a) and in (g) to (i) for the condition of (f). (e) Schematic diagram describes the molten metal flow pattern as a function of surface tension (γ) and temperature (T) in a negative surface tension gradient. (j) Schematic diagram describes the molten metal flow pattern as a function of γ and temperature T in a positive surface tension gradient [483].

Fig. 6.13. Experimentally measured concentration of aluminum [485] for the deposition of Ti-6Al-4 V by PBF-EB.
approximately 10 and 30, and the processing conditions to create a given microstructure can be related to this value. For example, to create a single-phase $\beta$-titanium microstructure at room temperature, a metastable titanium alloy with a low Mo-equivalent would need to be cooled or quenched more rapidly from the high-temperature $\beta$-phase field than an alloy with a higher Mo-equivalent. After quenching to metastable $\beta$, these alloys are typically heat-treated to precipitate a fine dispersion of the $\alpha$, plus possibly other phases, which act as a strengthening mechanism and partially stabilizes the alloy to further transformation. In conventional processing of wrought metastable $\beta$ titanium alloys, heat treatments can vary from a single temperature for stress relieving or annealing, to duplex or triplex temperature schedules with peak temperatures that may be above or below the $\beta$ transus, while cooling conditions can be varied to produce a wide range of microstructures and properties.

Alloy C, $\beta$C, $\beta$21S, and Ti-5Al-5V-5Mo-3Cr (Ti-5553) are some of the more prominent alloys, listed in order of highest to lowest Mo-equivalent. These alloys largely retain their bcc structure to room temperature due to their lower transus temperatures and the sluggish transformation to $\alpha$ owing to the lower diffusion rates of the $\beta$-stabilizing alloying elements. By definition, metastable $\beta$ alloys do not form $\alpha'$ martensite even on rapid cooling due to their higher alloy content and correspondingly lower $\alpha$ temperature and can be heat-treated to strength levels comparable to those for Ti-6Al-4V but with greater ductility and toughness when optimally processed [487,488]. Metastable $\beta$ alloys [487,488] typically have lower elastic moduli than $\alpha$ titanium, or near-$\alpha$ titanium alloys and are normally slightly denser owing to the additions of heavier $\beta$-stabilizing alloying elements. Their strength in the solution-annealed condition is modest and allows machining and forming before strengthening by heat treatment below their $\beta$-transus temperature (composition specific). In addition to strengthening by the formation of $\alpha$ phase, and precipitation of other phases that include $\beta'$ and $\omega$ during heat treatment, with $\omega$ phase potentially being a precursor to $\alpha$ phase formation also affects the strength and ductility of the final component [489].

The Fig. 6.14 shows optical micrographs of a metastable $\beta$ phase Ti-5553 alloy that has been laser powder bed processed and heat-treated to different conditions [490,491]. In the as-built, and stress-relieved condition at 300 $^\circ$C shown in Fig. 6.14 (a), the microstructure at this magnification appears as single-phase grains that are patterned and multi-sized due to the nature of the layer-by-layer LPB process [490]. If this alloy had been rapidly quenched from the $\beta$ phase field, this microstructure would be 100% $\beta$, however, in the as-built or stress-relieved condition, there may be secondary phases in the microstructure that are too small to be observed at these

![Fig. 6.14. Backscattered electron images of PBF-L processed Ti-5Al-5V-5Mo-3Cr showing (a) stress relieved condition at 300C, and b-d) heat treated to higher temperatures [490]. Precipitates of $\alpha$ phase become visible at (b) 600 $^\circ$C and coarsen at (c) 700 $^\circ$C and (d) 800 $^\circ$C [490]. The $\alpha$ phase (dark) forms on grain boundaries and is also dispersed throughout the $\beta$ grains.](image-url)
magnifications. Upon heat treatment at higher temperatures, the α phase nucleates, grows, and becomes visible at 600 °C (Fig. 6.14(b)) and above, where it is observed to be present both within β grains and along the β grain boundaries. As the heat treatment temperature increases to 700 °C (Fig. 6.14(c)) and 800 °C (Fig. 6.14(d)), there is a coarsening of the microstructural features and an increase in the size of the α phase. At 800 °C the microstructure consists of approximately 25% α in what appears to be a β phase matrix, thus there is an optimum post-build heat treatment for this alloy since these microstructural features affect both strength and ductility.

The use of metastable β alloys has been focused on two principal areas of application: (1) for traditional aerospace components, as summarized by Cotton et al. [486], and (2) for biomedical purposes such as implants and prosthetic devices [487]. The development of metastable β alloys for aerospace applications preceded their consideration for bio-medical use. These efforts led to the commercialization of several successful alloys including β-C, β – 21S, and Ti15V3Cr3Sn3AI. Ti alloys are bio-inert and are often selected for biomedical applications including various implants. The development of metastable β alloys for biomedical applications followed a two-stage path with time [488]. Initial efforts in the bio-medical field were aimed at (α + β) Ti-6Al-4 V alloys but issues with their higher modulus caused issues with stress shielding and loosening with attendant failure issues [488]. This concern prompted biomedical researchers to turn to metastable β alloys owing to their lower moduli. During this first stage, alloys used for aerospace were natural starting points. The focus of alloy development was on lowering the modulus of metastable β alloys to match more closely with that of bones (~30 GPa) to avoid stress shielding. However, these alloys could not achieve both low modulus and high strength. This issue led to research aimed at finding alloys with low modulus and high strengths in the second stage of development, often containing considerable Nb content.

PBF-EB of the β alloy Ti-24Nb-4Zr-8Sn formed [492] a lamellar α” (orthorhombic Martensite) phase in the β matrix with a specific orientation relationship between the two phases, [100]β // [100]α”. The presence of the α” produced high hardness and strength but can lead to poor fatigue properties. The hardness of the material was ~ 25% greater than that of an arc melted alloy. PBF-L of Ti-24Nb-4Zr-8Sn scaffolds for biomedical applications has been performed by Li et al [493]. Production of scaffold structures has also been considered to provide stiffness matching with bones with Ti-6Al-4 V. The porous scaffolds also assist with bone integration (osseointegration) and contribute to better implant performance since it permits control of component stiffness to match the bone modulus. Issues with the evaporation of Sn (high vapor pressure) in the β alloy caused porosity in the scaffolds which caused the fracture of some of the struts on straining. Development of alternate alloys with little or no Sn may prove helpful. The presence of unmelted particles also contributed to strut failure [493].

Ti-26 Nb β alloy parts were made by DED-L by Wei et al. [494]. Heat treatment after deposition at 650 °C (sub-transus) revealed the presence of some α-phase which disappeared above 850 °C (supra-transus). Like in the last study, unmelted Nb particles were found in the as-deposited sample due to the low laser power (750 W) used for this study. Some solidification segregation was also visible in the deposits, as seen in the micrographs in Fig. 6.15. The position of α peaks in the XRD spectra shifted to lower values of diffraction angle (commonly called 2θ) with annealing due to Nb dissolution which caused an increase in lattice parameter. The extent of Nb dissolution increased with increasing heat treatment temperatures. Fine acicular αS was found in the inter-dendritic regions after heat treatments

![Fig. 6.15. Microstructure of annealed samples of DED-L of Ti-26Nb β alloy at different temperatures for 0.5 h (a) 650 deg. C and (b) 750 deg. C. (c) and (d) are the high magnification images of (a) and (b), respectively [494].](image-url)
due to the residual effects of segregation. High strength was achieved in Ti-35Nb-7Zr-5 T (a metastable β alloy) parts made by PBF-L by Raghunandan et al. [495]. The presence of geometrically necessary dislocations (GNDs) near grain boundaries from fast cooling and (200) texture of the β grains were claimed to contribute to the high strength. The as-deposited microstructure was characterized by a cellular solidification microstructure. In addition, DED-GMA of a metastable β alloy called β-C [496] and DED-GMA of Ti-35Nb-15Zr metastable β alloy [497] have also been reported. Several strategies to control grain structure, phases, and defects during AM of these alloys are discussed below.

6.2.2. Control strategies for grain structure, phases, and defects

Metastable β alloys have been used to fabricate components using different processes such as PBF-L, PBF-EB, DED-GMA, and DED-L where the part temperature fluctuates with layer-by-layer processing conditions. Because of this and the sensitivity of these alloys to heat treating, the alloy composition and processing conditions are critical in producing a component with the desired as-built or post-build heat-treated properties for optimum performance. In addition, since these titanium alloys, in general, tend to have low ductility, they are particularly sensitive to internal defects that may cause stress concentrations, reduce strain to failure, and reduce fatigue life [492,493].

Heat treating of metastable β alloys can precipitate α phase at the grain boundaries and interior of the grains. These effects have a strong influence on mechanical properties as illustrated in Fig. 6.16 for a PBF-L processed Ti-5553 alloy [490]. Initially, in the as-built condition, the alloy has a moderate ultimate strength of about 800 MPa, with good ductility and nearly 18% elongation to failure. Heat treating at temperatures in the 400–600 °C range for 1 hr, increases strength above 1,000 MPa, but the ductility drops to below 2%, which is not acceptable for most engineering applications, and there are associated large changes in the elastic modulus. Heat treating to higher temperatures overages the microstructure, recovering some of the ductility with a corresponding loss in strength, and places the microstructure in a more stable condition. Bakhshivash et al. [498] demonstrated this on a Ti-5553 build using different heat inputs as defined by a volumetric energy density (VED, measured in energy per unit volume of melted metal, of the PBF-L processing parameters. Low VEDs produced substantially single-phase β microstructures with small amounts of ω phase, while higher VEDs aged underlying layers of the build. At medium VED, the build has a consistent hardness of approximately 300 Vickers, but at high VED only the topmost layers have this hardness, while lower layers in the build have α phase precipitates and Vicker’s hardness values of approximately 500 due to significant aging during the build.

One solution to preventing the overaging of metastable β alloys during the build is to limit the heat input. However, several tradeoffs must be considered. First, lower heat inputs typically slow the build speed and increase the part cost. The lack of fusion defects can form if insufficient heat is present to properly remelt previous tracks. Fig. 6.17 shows a typical lack of fusion defect in a PBF-L processed Ti-5553 alloy [491], which would affect the mechanical properties of the joint. Therefore, optimization of printing parameters is critical for metastable β titanium alloys to avoid defects on the low heat input end, and avoid the formation of α phases on the high heat input end of the processing parameter window. Fig. 6.17 further shows another important consideration, which is surface roughness. In this part, the thin vertical truss element has ridges and valleys with ~ 0.1 mm surface roughness with additional powder particles attached. This roughness creates stress risers which are undesirable but can be improved using lower heat inputs. For example, it is found that the surface roughness significantly varies for a PBF-L Ti-5553 part manufactured with low, medium, and high VED [498]. It is clear that surface roughness improves with lower VED, but this effect also needs to be optimized to avoid the lack of fusion defects at lower heat inputs.

Fig. 6.16. The effect of heat treating in the 400–600 °C range for 1 h on the mechanical properties of metastable Ti-5Al-5 V-5Mo-3Cr PBF-L alloy showing an increase in strength and corresponding dip in ductility, with corresponding changes to the elastic modulus [490].
provides opportunities to repair defects in AM parts and join smaller AM parts together to make structures larger than can be built in a powder bed. Pulsed laser beam welding of the Ti-5553 component at a short pulse duration was performed [490] where the fusion zone of the weld was defect-free with what appears to be a single phase $\beta$-titanium microstructure [490,491]. The fusion zone grains grow epitaxially from the AM base metal microstructure as would be expected for a fusion weld, with what appears to be minimal heat-affected zone changes to the surrounding AM microstructure. Marvel et al. [499] produced electron beam welds in a metastable $\beta$-Ti-5553 alloy at slower cooling rates, where in situ aging produced precipitation of $\omega$ and $\alpha$ phases in the microstructure of both the weld and base metal regions. Post-build heat treating to recover the microstructure is possible, but complicated multi-stage heat treating schedules may be required [499]. Such post-build heat treatments of AM components are dependent on the initial AM processing parameters and the specific alloy composition but may be required to achieve optimal metastable $\beta$ titanium properties.

7. Control of grain structure, phases, and defects in copper alloys

Copper and copper alloys are used for many different types of applications that make use of copper’s exceptional thermal and electrical conductivity, as well as its ability to form high-strength, wear-resistant, and corrosion-resistant alloys [500]. However, pure copper can be difficult to deposit by welding [501] and can be difficult to additively manufacture because its high thermal conductivity rapidly draws heat away from the melt zone [502,503]. Creating a melt pool in copper requires intense heat sources to counteract its high thermal conductivity, and the ensuing rapid cooling of the melt pool often results in macroscopically rough solidified surfaces. Other challenges for producing AM parts from copper include the high solubility of oxygen in liquid copper, which causes porosity in melt zones, and copper’s high reflectivity to infrared laser wavelength radiation, which reduces energy absorption during laser-based AM processes. Nevertheless, progress has been made in developing additively manufacturing high purity copper, copper alloys, and functionally graded composites containing copper.

7.1. Strategies for grain structure, phases, and defect control in high purity copper

Components that require high thermal and electrical conductivity use high purity copper because even small amounts of many impurities lower the conductivity [500]. Some exceptions exist where small amounts of elements such as Cr are added for strength or second-phase particulates such as alumina are added for high temperature creep resistance [500]. The copper feedstock needs to be deoxidized and free of copper oxide phases to minimize porosity formation in the melt pool, and oxygen-free high conductivity (OFHC) copper, which is available in both powder and wire forms, is often used for PBF and DED applications. Copper components such as metal injection tool molds, semiconductor cooling applications, and other heat exchanging devices are targeted areas for PBF-L [503,504] and PBF-EB [505,506] where higher powers may be required compared to other metals and alloys [3,507]. In addition, shorter laser wavelengths are beneficial for laser processing due to the poor coupling of infrared laser wavelengths that are typically used in PBF-L [502], and low powder bed temperatures are required due to the tendency for high purity copper particles to sinter.
together [506].

Even with high purity powders, substantial porosity of > 20 vol% has been observed in PBF-L fabricated copper components [502,503]. Fig. 7.1 shows an example of this porosity, which both reduces the mechanical integrity of the component and lowers its bulk thermal properties. This type of porosity is most frequently related to the difficulties of keeping a steady and continuous melt pool established and incomplete wetting into preexisting layers, leaving the lack of fusion defects in the microstructure. Through careful PBF-L processing parameter development, porosity and lack of fusion defects in pure copper can be significantly reduced but porosity is difficult to eliminate. DED-GMA using wire feedstock of OFHC copper can be used to manufacture components from copper but requires significant attention to the processing parameters for starting and maintaining a stable melt pool, particularly before the part reaches a steady-state preheated condition when wetting into previous layers can be difficult. Fig. 7.2 shows a cross-section through a DED-GMA wall built from OFHC copper where spherical porosity exists and is common in these builds. If required, hot isostatic pressing is successful in reducing porosity and producing more dense parts in binder-jet fabricated pure copper and may be useful to close internal voids made by other AM techniques.

7.2. Strategies for grain structure, phases, and defect control in copper alloys

For applications where strength and corrosion resistance is desired, copper is alloyed with Sn, Zn, Ni, Al, Si, and other elements to create a variety of high strength, wear-resistant, and corrosion-resistant alloys in the bronze, brass, and cupronickel alloy systems [500]. Additive manufacturing of copper alloys faces similar challenges as pure copper, with the additional complexity of alloying element segregation and the potential for cracking in some alloy systems. Many different AM methods have been used to produce copper alloy components including PBF-L [502,508–513], PBF-EB [514–516], DED-GMA [517–525], and DED-L [526] with varying degrees of success. Bronze alloys of different compositions manufactured by PBF-L tend to be stronger than their cast counterparts due to the refinement of the microstructure created during the high cooling rates associated with PBF-L [3,508,512,513]. Post-build heat treating of PBF-L Cu-Sn bronze and DED-GMA bronze samples further increases the strength and ductility of the alloy through solid solution strengthening and have properties comparable to conventionally processed materials [508,512,527].

PBF-L was used to fabricate structures from a Cu-Ni-Sn alloy which displayed a highly refined microstructure with grain boundary precipitates that strengthened the alloy with favorable ductility so that it could be used in the as-built condition [513]. Nickel aluminum bronze (NAB) is a Cu-Al-Ni alloy commonly used for naval applications due to its high strength and corrosion resistance in seawater, and forms a martensitic microstructure during PBF-L that requires higher temperature heat treating for optimum performance, but when properly built and heat-treated can equal the properties of cast and wrought NAB alloys [510]. Precipitation hardening copper alloys containing small amounts of Cr, Zr, and Ti can be processed with small amounts of porosity at 97.9% density by PBF-L and subsequently heat-treated for increased strength [511]. The columnar grains in bronze alloys tend to grow parallel to the build direction in both PBF-L and DED-GMA and create higher strength properties parallel to the build direction than perpendicular to the build direction [511,527]. Fig. 7.3 (a) shows the microstructure of a DED-GMA silicon-bronze (3%Si-Cu) alloy wall where the elongated grains can be seen growing upward in the build direction [528]. A similar texture is seen in PBF-EB fabricated bronze alloys [514–516]. Reduced strength and ductility relative to conventional hot rolled and heat-treated alloys are sometimes attributed to porosity in the sample that may be reduced by subsequent hot isostatic pressing [511].

Many conventionally manufactured bronze components are castings that are physically too large to be made in powder beds and require higher deposition rates than are possible by PBF. Alternative DED wire-based (DED-GMA and DED-EB) [141] and powder-based DED-L [3] are high deposition rate processes that ideal for large AM parts since they do not have size restrictions of powder beds. The majority of the DED work has been performed using DED-GMA on NAB alloys with typical compositions containing Cu9% Al5%Ni plus other minor alloying elements to enhance strength or corrosion resistance [518–525]. Even higher deposition rates are
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being developed using dual wire rather than conventional single wire DED methods [523]. Dual wire processes are also being explored for in-situ alloying using DED-GMA [522] and also DED-EB [529] processes. A DED-GMA build microstructure produced by in-situ alloying with two dissimilar metal wires is shown in Fig. 7.3 (b), where a transition from an OFHC copper build to an in-situ alloyed Cu-6 wt.% Ni alloy was produced. In this case, a cold Ni wire was fed into the copper GMA melt pool at a controlled rate to

Fig. 7.2. An optical micrograph of oxygen-free high conductivity copper processed by DED-GMA showing spherical porosity that is commonly observed and difficult to eliminate (as polished) [528].

Fig. 7.3. (a) An optical microstructure of DED-GMA deposited silicon-bronze with columnar grains growing upward, parallel to the vertical build direction (etched in dilute nitric acid) [528]. (b) An optical micrograph of an in situ Cu 6 wt.%Ni alloy specimen created by a DED-GMA dual wire process with Ni being added to the copper GMA melt pool using a secondary Ni cold wire feed at a controlled wire feed rate. Porosity is present and is similar to what is observed in pure copper (etched with FeCl$_3$ in HCL aqueous solution) [528].
produce the desired composition [528]. Nickel will alloy with copper, being miscible in both the liquid and solid phases, and the microstructure has both nickel and copper rich regions due to the high melting point of nickel and incomplete homogenization in the weld pool during cooling to room temperature. Practical limits for this process in Cu-Ni are approximately 3–12 wt% Ni, where higher Ni alloy content would require a preheated hot-wire for homogeneity. Some porosity is present in the microstructure, particularly near the edge of the melt pool in this sample.

The wire-based AM processes are very similar to welding [141] and many bronze alloy welding filler metals have been developed that tend to work well in AM processes, producing dense 3D AM parts without cracking and minimal porosity. Fig. 7.4 shows the microstructure of an aluminum bronze alloy (6.6%Al-Cu) wall produced by DED-GMA [528]. This alloy builds very well with no cracks in thin walls and does so with minimal porosity, but it does form columnar grains along the build direction. The typical DED-GMA microstructure of copper alloys shows a degree of microsegregation and/or second-phase formation as seen in silicon bronze (Fig. 7.3 (a)). Post-build heat treating is sometimes used to homogenize the microstructure and reduce the number of intermetallic phases that form at grain boundaries for improved strength and ductility [521,522]. Such heat treatments are also used in attempts to reduce mechanical anisotropy related to the large columnar grains that form in the build [525,527]. Ultrasonic vibration during the DED build has been explored as a means to break up the columnar grain structure and build at lower inter-pass temperatures to reduce anisotropy [519]. It should be noted that not all bronze alloys will build without problems and that brittle intermetallic phases, or low melting point compounds can form during the build which will result in cracking [530,531]. One example is shown in Fig. 7.5 where a 3%Si bronze alloy was deposited using DED-GMA in a thin-wall bowl-shaped part configuration which developed cracks in the columnar grain boundaries. The cracks traversed many layers parallel to the build direction [528].

8. Functionally graded materials

Functionally Graded Materials (FGMs) refer to materials with spatially varying properties through gradual changes in composition and microstructure. AM is well suited to produce FGMs owing to its two intrinsic features: the layer-upon-layer printing process, and the selective melting of spatial regions where the scanning strategies and printing parameters can be readily altered. AM of FGMs can create components in ways not easily achievable by conventional manufacturing. These components including bimetallic joints and graded transitions have important commercial applications that can benefit from multi-material performance in some cases and cost savings in others. Additionally, FGMs fabricated by AM have been explored for high-throughput testing of material properties such as radiation damage in stainless steels [532], magnetic, electrical, and mechanical properties of Co-Fe-Ni alloys [533], and corrosion behavior of stainless steels [534].

![Optical micrographs of columnar grains forming in DED-GMA 6.6%Al-Cu bronze alloy.](https://example.com/fig7_4)
This section is focused on metallic FGMs produced by AM using multiple feedstock materials, which is an area for increased research activities. As it has been the subject of several recent review articles [3,4,535–538], the section provides a succinct review of printing FGMs using the five feedstock materials discussed in the previous sections, i.e., steels, aluminum alloys, nickel alloys, titanium alloys and copper alloys. Additionally, recent advances in printing functionally graded copper composites are critical reviewed and used as an example to illustrate the common challenges in controlling phases and defects in printing FGMs.

8.1. AM methods for printing functionally graded materials

FGMs fabricated by AM can be achieved using a single or multiple (two or more) feedstock materials. For a single feedstock material, altering the local composition during printing has been achieved by adjusting beam energy to evaporate volatile elements (e.g., Al in Ti alloy) [539,540] or modifying shield gas composition (e.g., the addition of N2) to induce gas-molten metal reactions [541,542]. Clearly, the composition range that can be varied using a single feedstock material is limited. On the other hand, AM using multiple feedstock materials, commonly referred to as multi-material additive manufacturing, can achieve wide composition and microstructure gradients.

Between the two most widely used AM processes for metal printing, DED is much more amenable to using multiple feedstocks than PBF. For example, different mixing ratios of feedstocks can be readily achieved by adjusting the feed speed of dual wires in DED-GMA.
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high hardness due to the formation of Ti₃Al intermetallic phase and exhibited brittle failure modes during compression tests.

For PBF of FGMs, advanced powder spreading systems are necessary to dispense powder particles of different materials onto the powder bed. Wei and Li reviewed various powder spreading systems for multi-material PBF-L such as a blade-based dual powder recoater and an ultrasonic-based dual powder dispenser [535]. Fu et al. discussed the potential application of those powder spreading systems for PBF-EB under vacuum conditions [545]. Moreover, they demonstrated the feasibility of an interesting approach to producing Cu-W graded material, where Cu and W powders with different particle sizes were used and the layer thickness was varied to control the Cu/W ratio in a layer. The composition gradient is commonly realized along the build direction (i.e., 1D functional grading). Wei et al. developed a blade + ultrasonic hybrid powder spreading system equipped with a micro-vacuum powder suction device shown in Fig. 8.1 (a) [546]. They demonstrated the feasibility of realizing the composition variations within layers and along the build direction (i.e., 3D functional grading), as shown in Fig. 8.1 (b). Walker et al. also demonstrated 3D functional grading using a PBF-L machine equipped with special powder hoppers to place materials at specified locations and a vacuum pump to selectively remove the prior powder [547]. Printed structures with Ti to Ta grading in both the vertical and horizontal planes and compositional grading between Inconel 718 and GRCop-42 copper alloy [547 548] are shown in Fig. 8.1 (c-e). It is evident that Ta that has a higher melting point than Ti showed rough structure under the same heat input.

8.2. Common challenges for controlling microstructure in functionally graded materials

AM of FGMs using various dissimilar metal combinations involving steels, aluminum alloys, nickel alloys, titanium alloys, and copper alloys has been studied in the literature although the resultant part quality varies greatly depending on the specific combinations [535,537]. Similar to dissimilar metal welding, a primary challenge for AM of FGMs is the lack of metallurgical compatibility between some dissimilar metals. The AM processes work well when the metallurgy of the dissimilar metal combination is known to be compatible and can be accomplished without forming brittle intermetallic phases or low melting point alloys that can result in liquation cracking [549,550]. The issue of forming brittle intermetallics is particularly challenging for the dissimilar combinations of titanium alloys to steels, titanium alloys to nickel alloys, titanium alloys to aluminum alloys, and aluminum alloys to steels. For example, Zhang and Bandopadhay used DED-L to print bimetallic Ti₆Al₄V + Al12Si structures [551]. The transition region showed high hardness due to the formation of Ti₃Al intermetallic phase and exhibited brittle failure modes during compression tests.

A wealth of information about weldable alloys and compatible combinations is available in the existing welding literature where dissimilar metal welding, weld cladding, and weld surfacing consumables and procedures have already been developed for a wide variety of applications [552]. For traditionally non-weldable combinations of metals such as the aforementioned titanium to nickel alloys, intermediate layers have been used to prevent cracking or other defects at the interface in DED-L builds [553,554]. In these cases, AM parameter development tends to be more involved than when building similar metal parts to ensure good bonding and minimal defects in the dissimilar metal interface and the transition zone, but high-quality parts have been demonstrated using different methods to create bimetallic transitions in otherwise incompatible alloys.

Another main challenge for AM of FGMs arises from the large differences in two feedstock materials’ thermo-physical properties including melting temperatures, thermal conductivity, and coefficients of thermal expansion. Additionally, in laser-based AM processes, the laser absorptivity of the two constituent metal powders can be different. These differences have been attributed to causing various defects such as the lack of fusion, unmelted powder particles, porosity, and cracking in AM of FGMs, a problem especially prevalent for FGMs of copper alloys to steels and cooper alloys to nickel alloys [535]. One strategy for mitigating these defects is to utilize composition-dependent adjustment of process parameters such as increasing the heat source power as the composition is transitioned from lower to higher melting point alloys [537].

With the continued advances in AM hardware and scan strategies, printing defect-free, quality FGMs is increasingly realized. As these FGMs are put to service, they can be subjected to unique failure modes that are uncommon to single alloys fabricated by AM. For example, dissimilar joints of ferritic steels to austenitic stainless steels are common in structures used in chemical and power generation industries. From a metallurgical perspective, the two materials are compatible and mix together well. However, during long-term high-temperature service, it is well documented that carbon diffuses away from the ferritic side towards the austenitic side, resulting in the formation of carbidic in the austenitic side near the interface, which in turn promote creep cavity formation [555]. Zuback et al. studied the carbon diffusion kinetics in an FGM from 2.25Cr-1Mo ferritic steel to austenitic Alloy 800H [556]. It was found that the carbon diffusion rate was significantly reduced by replacing the dissimilar joints with the compositionally graded joints. Moreover, they pointed out the importance of optimizing the grading based on the chemical potential of carbon rather than carbon concentration itself since the chemical potential of carbon was not a linear function of composition.

Corrosion properties are important for the in-service performance of additively manufactured materials [557]. For single alloys fabricated by AM, corrosion properties have been studied for aluminum alloy [558], copper alloy [559], titanium alloy [560], etc. For FGMs fabricated by AM, galvanic corrosion which is common in dissimilar metal welds can be important. For example, Kong et al. studied the corrosion properties of nickel Inconel 718 alloy with different TiC contents printed by DED-L [561]. It was found that the corrosion rate increased slightly with increasing TiC content due to the galvanic effect. However, to date, galvanic corrosion of FGMs especially those between aluminum alloys and other dissimilar metals (e.g., steels) remains largely unexplored. Further research is thus needed to ensure that FGMs fabricated by AM do not fail prematurely in service due to the issues such as carbon migration and galvanic corrosion.
8.3. Functionally graded copper composites

Compositionally graded copper composites and bimetallic parts provide a means to transition the material composition and properties from copper or copper alloys to another metal [526,529,531,544,556,562-565]. Smooth graded transitions between the two dissimilar metals are accomplished using the DED-L powder method where the composition can be adjusted on multiple thin layers by altering the ratio of two or more powder feeders on each layer where they form an in-situ alloy in the melt pool [3,544,556]. Fig. 8.2 shows a transition from a 304L stainless steel base plate (bottom) to a copper/tungsten composite made by the DED-L process [566]. In this micrograph, copper and tungsten powders were mixed and deposited onto the stainless steel base plate in multiple layers to produce a graded density composite, similar to an aluminum/tungsten-particulate composite produced using the same technique [544].

More abrupt transitions can be made directly from one metal to copper or copper alloys by PBF or DED using a dissimilar metal...
build plate or using different feedstocks, to create bimetallic parts by wire or powder methods [3,526,531,562-564]. Wire-based DED additive manufacturing for bimetallic parts is developed directly from traditional welding methods using arc, laser, or electron beam heat sources to melt and deposit a dissimilar filler metal [141]. Examples include transitions from a steel substrate to silicon bronze alloy made by the DED-GMA technique [562], and stainless steel to copper AM transition using DED-EB [529]. Copper and copper alloy bimetallic joints are created between many different metal combinations. For example, maraging steel to a copper build plate [564], a Cu-Cr-Nb oxidation-resistant alloy to an Inconel 718 build plate [526], Inconel 625 to a copper build plate [563] using the DED-L process, and 316L stainless steel to a Cu-Sn bronze alloy using PBF-L with a dual powder arrangement [531] have all been demonstrated. Fig. 8.3 (a) and (b) show a DED-GMA transition between 308 stainless steel to silicon-bronze at low and high magnifications, respectively [528]. The transition region between the two alloys occurs over approximately 500 µm, which is less than the bead height for each deposited layer and is crack-free and porosity free. Although dissimilar metal transitions between bronze and stainless steel using DED-GMA have shown some propensity for cracking at the interface due to the formation of intermetallic compounds [549], this particular transition was crack-free, possibly as the result of low residual stress in the thin wall that was built in this case. Fig. 8.3 (b) also illustrates the elongated bronze grains that initiate very close to the transition region and grow vertically upward in the build direction.

The Fig. 8.4 (a) shows the microstructure of a 308L stainless steel to OFHC copper transition joint produced by DED-GMA [528]. The copper wets the stainless steel base metal, forming a braze-like interface between the two metals, and some of the stainless steel melts into the copper as can be seen by the gray-colored elements in the copper matrix. Other than the presence of some spherical porosity, the transition produced a sound crack-free part [528]. Fig. 8.4 (b) shows the globular morphology of stainless steel in the copper, and copper in the stainless steel, at higher magnification. The globular morphology indicates the presence of liquid phase immiscibility that can occur in Cu-Fe alloys where a metastable liquid phase miscibility gap is known to be present [567,568]. An unusual feature is that the stainless steel droplets can migrate up multiple weld beads during the build, and were observed near the edge of the build through > 10 copper layers, which could be troublesome for some applications where pure copper is desired.

In summary, challenges remain to produce fully dense parts and smooth surfaces in copper-based FGMs due to copper’s propensity to form porosity and because of its high thermal conductivity. The metallurgy of some copper alloys produces sound deposits with other alloys, while others can develop solidification-related cracking, so it is important to select known weldable alloys and ones that respond well to the AM process being used. The above examples of functionally graded copper composites printed by PBF and DED processes using powder and wire feedstocks underscore the common challenges in AM of FGMs especially those involving dissimilar metals with mismatched thermo-physical properties and limited metallurgical compatibility.
9. Emerging tools for controlling grain structure, phases, and defects

Mechanistic models have provided insight into the microstructure variations and defect formation based on scientific principles that could not have been achieved in any other way [1,4]. However, metallic materials are notoriously complex, and most mechanistic models are computationally intensive. However, analytical models are also used in the understanding of various aspects of microstructure as discussed in section 2. Currently, model-based understanding of the evolution of microstructures and defects has been rather limited. In addition, in many metallic systems, the physical processes in the evolution of microstructure and defects are still evolving. Furthermore, a specific defect such as cracking may originate from multiple mechanisms. As a result, mechanistic models cannot be built in many cases because of the lack of mechanistic understanding. In such cases, data-driven techniques such as machine learning, dimensional analysis, and statistical methods can provide important trends of the effects of process parameters on grain structure, phases, and defects often without the need for phenomenological understanding. This section reviews the applications of mechanistic models as well as data-driven techniques to control grain structure, phases, and defects in AM.

9.1. Mechanistic model-based control

9.1.1. Models to control grain structure

9.1.1.1. Phase-field model. Phase-field models are used to predict solidification structure during additive manufacturing. They solve the Allen-Cahn and Cahn–Hilliard equations and can track the interfaces of different phases. Sub-grain level features can be simulated for controlling solidification structures during laser PBF. For example, Park et al. [569] proposed a phase-field model to simulate the growth of dendrites during solidification of IN718.

Fig. 9.1. Dendrite growth during solidification of PBF-L of IN718 simulated using phase field model [570]. Results are shown with time for different solidification regimes: (a–c) columnar: $G = 2 \text{ K/m}$ and $R = 10^{-3} \text{ m/s}$, (d–f) mixed: $G = 10^4 \text{ K/m}$ and $R = 0.01 \text{ m/s}$, (g–i) equiaxed: $G = 100 \text{ K/m}$ and $R = 0.1 \text{ m/s}$.
solidification process during laser PBF of AlSi10Mg. The model considered both the epitaxial effect of the previously deposited layer and the deviation of the growth direction from the local heat flow direction. The knowledge of the grain structure evolution for a given set of processing conditions allows appropriate selection of processing conditions including the scanning strategy. Nabavizadeh et al. [570] developed a three-dimensional hybrid phase-field - lattice Boltzmann model to simulate columnar-to-equiaxed transition in Inconel 718 alloy during directional solidification (Fig. 9.1). Based on the model, a CET solidification map was developed for different temperature gradients and growth rates [570] which can be used to identify conditions to achieve the desired solidification morphology. Yang et al. [571] proposed a phase-field model to simulate the grain nucleation and growth in molten pools, epitaxial growth from powder particles, substrate, and previous tracks, grain re-melting and re-growth in overlapping zones, and grain coarsening in heat-affected zones during laser PBF of 316L [571]. The simulation of the spatiotemporal variations of the 3D microstructure by the phase-field model provides a useful route for visualization, which is challenging experimentally. The mechanisms for the formation and transition of various sub-grain and grain structures revealed by the simulations can be useful for the determination of control strategies targeting specific microstructures.

9.1.1.2. Cellular automata and Monte Carlo models. Modeling of microstructure during additive manufacturing using Cellular Automata mainly focuses on the solidification process [572–581]. The morphologies, sizes, and orientations of the grains have been simulated. For example, Koepf et al. [579] used a Finite-Element (FE) model with a Cellular Automata (CA) model to predict the microstructure evolution during PBF-EB of CMSX-4, as shown in Fig. 9.2 (a)-(c). Since the grain morphology and the texture could be calculated, the modeling provides a tool to connect process variables with the grain structure and texture. Li et al. [582] used a mesoscale Cellular Automata model with a macro-scale thermal model to predict the three-dimensional grain structure in the direct laser deposition process of stainless steel 304, as shown in Fig. 9.2 (d)-(e). It was found that the nucleation parameters (N0, the number of nucleating sites, ΔTc, the extent of undercooling) can significantly affect the grain structure. An increase of N0 and/or a decrease of ΔTc will encourage the occurrence of equiaxed grains, while a decrease of N0 and/or an increase of ΔTc will promote columnar grains.

Fig. 9.2. Grain growth and CET during solidification AM simulated using Cellular Automata: (a) 3D section view of the numerically predicted microstructure, (b) and (c) comparison of the simulated and experimental results with a longitudinal section cut [579]. (d) Differences in grain structure at different nucleation density [582]. (e) The G-V map was obtained with different values of N0 [582].

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The model is useful to study the effect of the variation in nucleation density due to the addition of inoculants or grain refiners on solidification morphology and grain growth. Mohebbi et al. [573] used the CA model to simulate the grain growth process during laser PBF of aluminum alloys. The formation of the bimodal grain structure was well reproduced, as shown in Fig. 9.3. Such well-tested CA models are valuable tools for understanding and predicting the microstructural evolution in laser PBF processes.

Fig. 9.3. Microstructures of PB-LBM processed (a) Scalmalloy® and (b) Al-Mn-Sc alloy, and (c) simulated microstructure of Sc-modified aluminum alloys [573].

Fig. 9.4. Evolution of grain structure simulated considering the localized solidification conditions at the trailing edge of the moving molten pool, and the solid-state growth due to multiple thermal cycles using the Monte Carlo method [36]. The results are for DED-L of Inconel 718.

The model is useful to study the effect of the variation in nucleation density due to the addition of inoculants or grain refiners on solidification morphology and grain growth. Mohebbi et al. [573] used the CA model to simulate the grain growth process during laser PBF of aluminum alloys. The formation of the bimodal grain structure was well reproduced, as shown in Fig. 9.3. Such well-tested CA models are valuable tools for understanding and predicting the microstructural evolution in laser PBF processes.
models can be used to identify processing conditions for achieving the desired grain structure during PBF of aluminum alloys.

Monte Carlo (MC) models were used to predict grain growth during additive manufacturing [36,583–586]. MC models are based on probabilistic approaches and are suitable for the simulation of grain boundary migration considering the variations of interface energies. However, grain growth during solidification largely depends on the solidification conditions determined by the moving molten pool. For example, Wei et al. [36] reported the comprehensive grain growth model considering both the solidification and the solid-state heating and cooling processes (Fig. 9.4). The transient solidification process was simulated considering the moving solidification front. Grain growth during ten layers of deposition is shown in Fig. 9.4 (a). Moreover, the evolution of the grain structure in the solid metal during repeated thermal cycles was simulated using an MC model. The calculations show the variation in the grain structures in various planes within a three-dimensional structure as shown in Fig. 9.4 (b)-(e). Rodgers et al. [585] simulated the grain growth during laser PBF of SS 316L parts on a scale of several millimeters with complex scan patterns used in AM (Fig. 9.5). It was found that columnar grains are both more likely to be elongated along the build direction and have a larger cross-sectional area perpendicular to the build direction at high laser powers. The three-dimensional variations of grain structure provide a key to understanding the anisotropic mechanical properties observed in additively manufactured parts.

The above results imply that the spatial variations of the grain structure can be simulated by high-fidelity 2D and 3D Cellular Automata and Monte Carlo models. Moreover, the transient solidification conditions, the resultant grain structure, and the solidification texture can be examined. The visualization of the simulated transient microstructural features in the 3D domain and virtually any 2D sections can provide valuable information that is difficult to obtain experimentally through the characterization of specimens. Thus, the use of mechanistic models for grain growth provides the ability to simulate grain structure and understand the effects of the AM process conditions.

### 9.1.2. Kinetic modeling of phase transformation to control phases

#### 9.1.2.1. Johnson Mehl Avrami model

The Johnson Mehl Avrami (JMA) model can describe the rate of phase transformation during the heating and cooling processes for the solid-state phase transformations [82,587 180,588,589]. JMA model uses analytical equations and applies to various alloys supported by corresponding materials properties and phase transformation parameters. For example,
Mukherjee et al. [180] predicted the transformation of martensite during laser DED of a tool steel using JMA kinetics and computed 3D, transient temperature fields [180]. Fig. 9.6 (a-d) show the temperature distributions on a selected plane and at a monitoring location ‘A’ in the first layer (Fig. 9.6 (e)). Considering the repeated heating and cooling cycles during the deposition, and the phase transformation kinetics, the hardness at various locations was predicted (Fig. 9.6 (f)) as a function of time. These models can compute the kinetics of phase transformations taking into account the multiple thermal cycles and they provide a means to understand the evolution of microstructure and properties.

Lu et al. [588] simulated the evolution of precipitates in IN718 during the DED-GMA process, using the JMA model. It was found that the distribution of micro-hardness in the mid-section of the sample was consistent with the distribution of $\gamma''/\gamma'$ strengthening phases fraction calculated by the model. More $\gamma''/\gamma'$ strengthening phases were present in the middle/upper region than in other regions, which indicates that proper transformation temperature and longer transformation time enhanced the transformation extent of $\gamma''$ and $\gamma'$ phases at the local region of the build. Since the JMA model uses analytical equations and does not capture the phenomenological features of the phases such as the morphologies and dimensions, other mechanistic models such as phase-field models are required for a more detailed understanding of the phase transformation processes during AM.

9.1.2.2. Phase-field model. Phase-field models can predict solid-state phase transformations. For instance, Shi et al. [590] used a phase-field model to compute the precipitation and dissolution of secondary-phase $\alpha$ ($\alpha'$) precipitate during repeated thermal cycles during laser PBF of Ti-6Al-4 V. Moreover, Shi et al. [590] developed a multiscale model integrating a powder-scale transient heat transfer and fluid flow model, a Cellular Automaton model for the simulation of solidification grain structure and texture, and phase-field modeling of precipitation and dissolution of secondary-phase precipitates during repeated thermal cycles [590]. It was found that successive layers exert a cyclic thermal influence leading to in situ decompositions of a near $\alpha'$ martensitic structure or precipitation of


the equilibrium \(\alpha\) precipitate. In other words, the formation of the secondary phases can be controlled by adjusting the thermal cycles via changing the heat source power, speed, layer thickness, and scanning pattern.

Although phase-field models have been applied to various aspects of microstructure control in AM, their engineering applications are restricted due to the low computational efficiency and the high computation cost. For example, the running process of the phase-field model with 17.88 million cells took 311 h for the simulation of a physical time of 0.009 s, using parallel computations on an NVIDIA Tesla M2090 GPU [571]. The intensive computational resources required by the phase-field models imply that considerable research efforts are still needed for the engineering applications of the phase-field models for real-time feedback for microstructure control.

9.1.3. Models for controlling defects

The mechanical properties of the AM parts are affected by the microstructure. On the other hand, defects such as lack of fusion, porosity, and cracking damage the integrity of AM parts on different scales, which adversely influence their mechanical properties. Therefore, it is critical to mitigate printing defects via experimental and modeling approaches. In situ observations of the printing process such as synchrotron XRD and high-speed imaging can obtain valuable data. However, the observation domain and correlated physical information are often incomplete due to the complex and highly transient nature of the AM processes. Mechanistic models are capable of revealing the highly transient physical processes involving the transport of mass, energy, and momentum on multiple scales. These underlying transport processes are helpful in the understanding of the formation and control of defects.

9.1.3.1. Models to control lack of fusion and keyhole pores.

The most common printing defects for all materials may be the lack of fusion and pores [1,4,591]. Fig. 9.7 shows several examples of lack of fusion during DED-L and PBF-L. It can be observed that such defects can occur on at least three scales: (i) the feedstock material scales such as powder-related voids for PBF [592] as shown in Fig. 9.7 (a); (ii) the track scale such as inter-track voids during DED [593] as shown in Fig. 9.7 (b), (iii) the layer scale such as inter-layer voids during PBF [594] as shown in Fig. 9.7 (c). Moreover, since the alloys have different thermophysical properties, the molten pool shapes and sizes for different alloys can vary significantly under identical process parameters, as shown in Fig. 9.7 (d). These differences in the molten pool shape and size make the susceptibility to lack of fusion to be different for different alloys. The inappropriate selection of hatch spacing and layer thickness would similarly cause a lack of fusion. The utilization of the mechanistic models can reveal the mechanisms of formation of lack of fusion and provide a means of avoiding the defects cost-effectively based on scientific principles.
Fig. 9.8. Keyhole-induced pores during PBF-L: (a)-(d) pores generated due to the oscillation of keyhole and molten pool [670].
Several examples of keyhole-induced pores in laser PBF products are shown in Fig. 9.8. A keyhole can be formed under the laser beam due to the action of recoil pressure. The instability of the keyhole may result in the formation of porosity. Note that the keyhole geometry may vary drastically due to the complex interaction of the laser beam with the powder feedstock and molten pool metal, with the absorption of the laser energy changing periodically as shown in Fig. 9.8 (a) and (b). Keyhole-induced pores are more frequently observed near the turning point of adjacent tracks (Fig. 9.8 (c) and (d)). With the help of high spatiotemporal resolution mechanistic models, it can be inferred that lower power or slower acceleration at the turn-around exit can prevent the above pores [595]. Fig. 9.9 (a) shows pores generated near the bottom of the printed track, in which condition process parameters were inappropriately selected. Fig. 9.9 (b) shows the initial generation and subsequent reformation of keyhole-induced pores in a typical multi-layer and multi-track condition [596]. These results prove that a sudden shut-off of the laser beam in the condition of a deep keyhole melting mode would cause various residual pores in the deposit during the layerwise printing processes. Adjustment of the processing conditions such as the laser power guided by an appropriate model can prevent the occurrence of keyhole-induced pores [597].

9.1.3.2. Models to control cracking. Modeling and experiments have shown that the crack propagation directions vary with scanning strategy and hatch spacings during laser PBF [99] (Fig. 9.10). Columnar grains grow in a curved pattern from the boundary towards the centerline of the molten pool. For small hatch spacings, only transverse cracks were observed. The absence of longitudinal cracks near the centerlines was due to the remelting of the centerline region with significant overlap. In other words, longitudinal centerline cracks were initially generated, but with the following elimination upon the printing of the subsequent adjacent track. Note that columnar grains in two adjacent tracks grew with different orientations [99] due to the bidirectional laser scanning strategy. Thus, the transverse cracks generated in each track exhibited opposite directions owing to the changes in the directions of motion of the molten pool and the resultant maximum heat flow directions at the trailing edges of the molten pools. The results show that the models can help control the grain structure and solidification cracking.

The Fig. 9.11 (a) shows the synchrotron x-ray imaging of the hot cracking behavior of AA6061 during laser PBF. It was found that hot cracks occur underneath the surface. The cracks originate near the back of the melt pool and the initial crack propagation speed is of order 1 m/s but decreases rapidly during crack propagation [598]. These results can provide valuable support for the validation of simulations of solidification cracking. Pores are favorable sites for crack initiation; while trapped-gas pores tend to form when the laser beam scans across the cracks when cracks are present in the material [598]. Modeling and experiments [599] have established the important effects of both the alloy composition and processing conditions on the evolution and control of solidification cracking during
It has been shown that model-based adjustment of the scanning speed, hatch spacing, and alloy composition can mitigate solidification cracking. The prevention of solidification cracking involves several factors including the chemical compositions of the alloy, the grain structure generated upon solidification, and the stress conditions during the rapid heating and cooling encountered during the AM processes [32,99]. Solidification cracking is affected by the specific chemical compositions and the resultant large intergranular liquid films at the final stages of solidification [600]. Therefore, adjustment of the chemical composition of the alloy can reduce the solidification cracking. For instance, Montero Sistiaga et al. [601] obtained a crack-free high strength aluminum alloy specimen with the addition of 4 wt% Si.

The generation of the cracks can be mitigated by controlling the grain structure and promoting CET. Parts with fine equiaxed grains are less susceptible to solidification cracking than those with coarse columnar grains [600]. Although promoting CET by modifying feedstock materials is an effective method of controlling solidification cracking [602,603], the modification of the chemical compositions of a given alloy may not be practical in many conditions. Therefore, it is worthwhile to explore other mitigation strategies such as process control guided by mechanistic modeling [99]. Another critical factor for the high solidification cracking susceptibility is the stress and strain conditions. High-fidelity mechanistic models for the quantitative assessment of these factors would be useful but they are still evolving.

9.1.3.3. Models to control composition change. During additive manufacturing of metallic materials, alloying elements vaporize from the molten pool. The rate of vaporization is the highest under the heat source where the temperature is the maximum. The vaporization is most pronounced for the electron beam processes because of the combination of low chamber pressure and high temperatures that
promotes rapid vaporization of alloying elements. All elements do not vaporize at the same rate due to their differences in vapor pressures. Selective vaporization of alloying elements often results in a significant change in the composition of the part from that of the feedstock[118,485,604]. Composition change is an important defect since it affects the microstructure, properties, and corrosion resistance.

It is well-known that composition change is significantly affected by the ratio of pool top surface area to pool volume. In addition, the rate of vaporization depends on the local temperature. Heat transfer and fluid flow calculations can calculate the molten pool dimensions and the temperature field since they affect the composition change. In addition, these calculations need data on the variations in the vapor pressure on elements with temperature. These calculation methods are well-established in the fusion welding literature [131] and can be adopted for the AM processes. For example, Knight’s model [605] was used to compute the change in the composition of alloying elements from SS316 during PBF-L, DED-L, and DED-GMA. A significant loss of manganese was observed followed by a less pronounced loss of chromium. It was shown how the model can be used to adjust laser power and scanning speed to reduce the composition change. A similar approach was also used to compute composition change in PBF-L of Ti-6Al-4V [606]. The temperature fields in the molten pool computed using a finite element method were combined with an evaporation model which computes the local vaporization rates of alloying elements. Aluminum was found to be the most susceptible to composition change.

There are very few models of additive manufacturing that consider vaporization and the resulting composition change of alloys. The rich knowledge base of composition change in fusion welding can help to develop such models for different additive manufacturing processes. Though the trends predicted by these models are also qualitatively observed in additive manufacturing experiments, rigorous validation of these models for a quantitative prediction of composition change remains to be undertaken.

9.2. Data-driven approaches

As discussed in the previous section, comprehensive numerical mechanistic models of grain growth and the evolution of phases have been used to understand the process and microstructure relationships to control grain structure and phases. In addition, there are physics-based models to control defects in AM parts. These models can provide accurate results but are often computationally intensive. Therefore, they often cannot be used in real-time. In contrast, data-driven techniques such as machine learning, dimensional analysis, and statistical methods are fast and can provide important trends of the effects of process parameters on grain structure, phases, and defects. Therefore, they are increasingly used since they are often easy to use, effective, and insightful.

Machine learning can make reliable and reproducible predictions [607–609] by learning from existing data. It can extract useful
Fig. 9.12. (a-c) An example of the application of machine learning in microstructure control [610]. The grain growth results (figure (a)) computed using a Monte Carlo model provide grain size versus frequency data in longitudinal and transverse directions (figure (b)). These data are used to train a neural network that could then calculate grain growth during DED- L (figure (c)).
Table 9.1
Examples of grain structure control in AM using several data-driven techniques.

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<td>A combination of artificial neural network-based ML and Monte Carlo grain growth model is used to control α grain size during DED-EB of Ti-6Al-4 V</td>
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<td>Image analysis and random forest-based ML are used to control the size of α grains during PBF-L of Ti-6Al-4 V.</td>
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<td>Dimensionless heat input is proposed and used to identify conditions to control secondary dendritic arm spacing in stainless steel 316 parts made by DED-L</td>
<td>[617]</td>
</tr>
<tr>
<td></td>
<td>Marangoni number is used to identify conditions to control the distribution of titanium carbide particles in the Inconel 625 matrix made by DED-L</td>
<td>[618]</td>
</tr>
<tr>
<td></td>
<td>Fourier number is used to identify conditions to control the cooling rates and solidification parameters during DED-L of stainless steel, Ti-6Al-4 V, and Inconel 718</td>
<td>[617]</td>
</tr>
<tr>
<td></td>
<td>Back of the envelope calculations using the Gaumann equation are used to control solidification morphology during PBF-EB of Inconel 718</td>
<td>[429]</td>
</tr>
<tr>
<td>Statistical methods</td>
<td>An analysis of variance (ANOVA) developed using experimental data is used to control the size of α grains during PBF-EB of Ti-6Al-4 V</td>
<td>[620]</td>
</tr>
<tr>
<td></td>
<td>An ANOVA developed using experimental data is used to control the size of both α and β grains during PBF-EB of Ti-6Al-4 V</td>
<td>[621]</td>
</tr>
<tr>
<td></td>
<td>An ANOVA developed using experimental data is used to control the size of α grains during DED-L of Ti-6Al-4 V</td>
<td>[622,623]</td>
</tr>
<tr>
<td></td>
<td>A non-linear regression developed using experimental data is used to control the grain size during PBF-L of AlSi10Mg</td>
<td>[619]</td>
</tr>
<tr>
<td></td>
<td>A linear regression developed using experimental data and results from a cellular automata grain growth model is used to control the size of β grains during DED-L of Ti-6Al-4 V</td>
<td>[624]</td>
</tr>
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</table>

Fig. 9.13. An example of the application of regression-based statistical analysis [619] for controlling the control the grain size during PBF-L of AlSi10Mg. The grain size data is extracted from the microstructure (figure (a)) and is used to develop the regression which is used to make a grain size process map (figure (b)).
information and relations from the data without any need for phenomenological understanding. The powerful, open-source codes for machine learning support their applications for solving many complex problems in AM including the control of grain structure, phases, and defects. There are two types of machine learning algorithms used in AM, supervised and unsupervised [608]. In supervised machine learning, variables are mathematically correlated to the material response such as grain size for microstructure prediction. The algorithm trained with both the input and output data can reveal the hidden relationship. The commonly used supervised machine learning algorithms for AM are neural networks, decision trees, Bayesian Networks, K-nearest neighbor, and support vector machines. Unlike supervised machine learning, unsupervised machine learning determines features from the data. It can be used to identify unique features from the digital images of the microstructure, such as classifying various types of precipitates during AM. In this subsection, applications of machine learning, dimensional analysis, and statistical methods to control grain structure, phases, and defects in AM parts are discussed.

9.2.1. Machine learning, dimensional analysis, and statistical methods to control grain structure

Features of grain structure in AM parts such as grain size, distribution and orientation, and dendritic arm spacing are used to train machine learning algorithms that can compute appropriate processing parameters to achieve the desired grain structure. Input data to
train machine learning can also be generated from well-tested mechanistic models of grain growth and the evolution of solidification structure. For example, Fig. 9.12 (a) to (c) provide an example of using the computed data to train a machine learning algorithm that is subsequently used to control the grain structure [610]. A 3D Monte Carlo-based grain growth model calculates the grain structure in
3D (Fig. 9.12 (a)). From the computed 3D grain structure, frequency versus grain size data are extracted (Fig. 9.12 (b)). These data are then used to train a neural network that could correctly and rapidly predict the grain size (Fig. 9.12 (c)). The well-trained neural network can predict the grain size the same as what is computed using the computationally intensive Monte Carlo model (Fig. 9.12 (c)).

Several examples [610–616] of the use of machine learning for grain structure control in AM are provided in Table 9.1. Although progress has been made in the applications of machine learning algorithms to control grain structure in AM parts, they are in their initial stages of development and need more research.

In AM, important variables often simultaneously affect the temperature field, cooling rates, and solidification parameters and thus the grain structure of the part. Therefore, combinations of multiple variables in dimensionless forms are often used to understand the evolution of the grain structure of AM parts [617]. These dimensionless variables reduce the number of parameters that need to be investigated. In addition, these variables express important physical meanings that cannot be represented by any single variable. Commonly used dimensionless numbers for grain structure control in AM [429,617,618] are indicated in Table 9.1.

Factors affecting the microstructure of AM parts such as thermal cycle, cooling rates, and solidification parameters are significantly impacted by the rate of heat dissipation from the part as well as the heat storage in the component. A dimensionless Fourier number \( F \) is defined as the ratio of the heat dissipation rate to heat storage rate as [617]:

\[
F = \frac{\alpha}{VL}
\]  

(12)

where \( \alpha \), \( V \) and \( L \) indicate the thermal diffusivity, scanning speed, and characteristic length, respectively. The characteristic length is often taken as pool depth [617]. An AM process with a high Fourier number exhibits rapid heat dissipation and fast cooling that can result in a fine grain structure [617]. In addition, a low Fourier number in AM process results in a small ratio of the temperature gradient to solidification growth rate which favors the formation of equiaxed grains [617].

Cooling rates during solidification, temperature gradient, and solidification growth rate that affect the solidification structures are affected by the shape and size of the molten pool. It is well-known that the molten pool shape and size are impacted by the molten
metal convection often quantified by the dimensionless Marangoni number \[617\] .

\[
Ma = -\frac{d\gamma}{dT} \frac{w \Delta T}{\mu a}
\]  

(13)

where \(\mu\) is the viscosity, \(\alpha\) is the thermal diffusivity of the alloy, \(w\) is the characteristic length of the molten pool, which is taken as the width of the molten pool, \(\Delta T\) is the difference between the maximum temperature inside the pool and the solidus temperature of an alloy, and \(\frac{d\gamma}{dT}\) is the sensitivity of surface tension gradient with respect to temperature. The vigorous convective flow of the molten metal characterized by a high Marangoni number can often break long columnar grains and the fragmented grains can act as heterogeneous nucleation sites for the equiaxed grains.

Solidification morphology depends on the ratio of the temperature gradient \((G)\) and solidification growth rate \((R)\). The values of \(G\) and \(R\) can be computed from a well-tested heat transfer and fluid flow model. The values of these parameters can be used in an experimentally determined morphology map such as Fig. 2.1 in section 2 to determine the morphology. Analytical calculations have also been proposed to predict the solidification morphologies such as the one proposed by Hunt [31]. Other equations have also been proposed such as the Gaumann equation to estimate the ratio \(G^2/R\) \[429\]:

\[
\frac{G^2}{R} = \frac{a}{n + 1} \left( -\frac{4}{3} \frac{a N_0}{\phi} \frac{\beta}{\alpha} \right)^{1/3}
\]  

(14)

where \(a\), \(n\), and \(\phi\) are alloy-specific constants. Depending on the alloy used, \(a\) varies between 1 and 10 K²s/m, and the value of \(n\) is generally 1 or 2 and \(\phi < 0.0066\) for fully columnar grain growth. \(N_0\) is the nucleation density whose value is in the order of \(10^{14} \text{ m}^{-3}\). \(\frac{\alpha}{\beta}\) and \(\frac{\beta}{\alpha}\) have threshold values that determine the columnar to equiaxed transition. However, the accuracy of these calculations depends on the correctness of the values of the constants that are not generally available for many alloys.

Statistical methods such as linear and non-linear regressions and analysis of variance are often used to control the grain structure. For example, Fig. 9.13 shows that a regression-based statistical analysis [619] was used for controlling the grain size during PBF-L of AlSi10Mg. The grain size data is extracted from the microstructure and is used to develop the regression which is used to make a grain size process map. Such process maps can guide engineers to adjust important variables to control grain size. Several examples [619–624] of the use of statistical methods for grain structure control in AM are provided in Table 9.1.

9.2.2. Machine learning and dimensional analysis for controlling phases

Machine learning [614,625–627] has been used to control the formation of secondary phases that affect the mechanical properties and corrosion resistance of additively manufactured parts. For example, Fig. 9.14 shows how SEM images of Ti-6Al-4 V parts made by PBF-L were used in image processing-based machine learning to control the formation \(\alpha\) phase and its size and distribution [614]. The SEM images in the figure show two phases \(\alpha\) and \(\beta\) with different contrasts. The ratio of the area of the two phases was evaluated by random forest-based machine learning. It could classify each image pixel to the particular class with the highest probability. After image segmentation using random forest, the missed borders (grain boundaries) between the \(\alpha\) and prior-\(\beta\) phases were reconstructed by using an additional image processing technique. It facilitated the visualization of the individual \(\alpha\) particles. Then, ellipses were fitted into each segmented \(\alpha\) particle and their minor axis values were estimated and averaged for all particles in the analyzed images. The size of the \(\alpha\) phases was then correlated to the processing conditions. This method provided a helpful way to control the shape, size, and distribution of the \(\alpha\) phase.

![Diagram](image-url)

**Fig. 9.18.** An example of using closed-loop control for in-situ control of microstructure. Here, A charge-coupled device (CCD) camera and an infrared (IR) camera were used to monitor the AM process. The sensing signal was sent to a real-time control system that provided a control signal to the machine to adjust the process parameters for in-situ microstructure control.
Dimensionless numbers are also used to control the formation of phases in AM parts. Heat input which is the ratio of heat source power to scanning speed significantly affects the temperature field, cooling rates, and solidification parameters and thus has a profound impact on the microstructure of AM parts. A dimensionless heat input ($Q^*$) is proposed as [617]:

$$Q^* = (P/V)/(P_R/V_R)$$  \hspace{1cm} (15)

where $P$ and $V$ refer to the laser power and the scanning speed, respectively. $P_R$ and $V_R$ represent the reference laser power and scanning speed that provide the lowest heat input per unit length among the range of process parameters. The dimensionless heat input, $Q^*$, indicates a measure of the energy supplied per unit length of the part. High heat input results in a slow cooling that allows sufficient time for the growth of the laves phases in nickel alloys (Fig. 9.15 (a-b)). The laves phases are hard and brittle secondary phases that significantly degrade the mechanical properties of AM parts [628–631]. Dimensionless heat input can help to select the optimum combination of power and speed to minimize the formation of the harmful laves phases [617].

9.2.3. Reduction of defects using machine learning

Common defects in additive manufacturing such as balling, cracking, porosity, lack of fusion, distortion, and surface roughness are often controlled by using machine learning. For example, a support vector machine-based machine learning was used to minimize the lack of fusion defects in Ti-6Al-4 V parts fabricated using DED-L [632]. Fig. 9.16 shows that the temperature field during the DED-L process was monitored using an IR camera. A molten pool boundary was extracted from the temperature field by tracking the solidus temperature contour. A support vector machine was trained using the data extracted from the molten pool results. The trained support vector machine was used to classify the processing conditions into two categories, normal and abnormal, based on the probability of lack of fusion defect formation. Defects were found in the components printed using the abnormal processing conditions responsible for the defect formation.

Machine learning was also used to reduce balling defects during PBF-L [238]. Fig. 9.17 shows that the machine learning algorithm was trained using both the experimental data on balling formation as well as several computed variables that represent the mechanism of balling formation. These variables were calculated using a heat transfer and fluid flow model. A balling susceptibility index was proposed and derived using the machine learning results that provided a threshold value delineating the defect and no defect cases. The index was proved to identify conditions for reducing balling defects during PBF-L of several engineering alloys. In addition, feature selection-based machine learning was used to provide the hierarchical influence of important variables on the balling defect. This hierarchy is helpful to guide engineers about which variables to tune in for controlling balling defects.

Examples of reducing defects in AM parts using machine learning include the control of the anomalies in powder spreading by a recoater during powder bed fusion [633]. In this case, a neural network-based machine learning was used to correlate the imperfection of the powder bed resulting from recoater streaking and hopping with part defects. The use of image processing and pattern recognition-based deep learning methods are increasingly used to control defects in AM. For example, an image processing-based technique was used to detect anomalies during the powder spreading of PBF-L to control defects [634]. In all of these aforementioned examples, machine learning has provided useful guidelines to control the common AM defects, the physics behind the formation of which is often not known.

9.3. In-situ control of grain structure, phases, and defects

As discussed, in the previous sections of this review, grain structure, phases, and defects are primarily controlled by alloy design, post-processing, and adjusting the processing conditions guided by experimental trials, mechanistic modeling, or data-driven techniques. However, in-situ control methods are also becoming increasingly popular where grain structure, phases, and defects are controlled during the printing process. Primarily, there are three main methods for in-situ control: (1) in-situ alloying [635–639] where alloying elements, inoculants, or grain refiners are added during printing to control the grain structure and phases, (2) application of external agitation during printing such as ultrasound [27,640–645], mechanical vibration [302,646,647], magnetic field [648–651], and external heating [652,653] to control microstructure and defects, and (3) in-situ adjustment of processing conditions [654–663] using a closed-loop feedback system. Applications of these three methods to control grain structure, phases, and defects are reviewed below.

In the in-situ alloying process [635–639], elements, inoculants, or grain refiners are added to the molten pool in powder form. Powders of high melting point elements, ceramic particles, and grain refiners are added to break the long columnar grains into smaller equiaxed grains to improve mechanical properties and reduce solidification cracking. For example, this process is used for grain refinement in AM of stainless steel 316 [637] and Ti alloys [638]. However, the addition of powders during a process with very rapid scanning needs precise control. External agitation such as ultrasound [27,640–645], mechanical vibration [302,646,647], magnetic field [648–651], and external heating [652,653] are used during printing to control microstructure and defects. Ultrasonic treatment is used to break long columnar grains to improve mechanical properties and prevent solidification cracking in stainless steels, titanium alloys, and nickel base superalloys [27,642–645]. Mechanical vibrations [302,646,647] are also used for the same purpose. Mechanical vibrations are easier and cheaper to use than ultrasonic vibrations. However, precise control of the vibration amplitude and frequency can be done using ultrasound. External magnetic fields used in DED-GMA [649,650] affect the arc source and thus the heat input and cooling rates to alter the grain structure and phases. Magnetic fields in laser AM processes [648,651] affect the molten pool shape and size and controls the cooling rate and solidification parameters. Application of external heating [652,653] using an auxiliary heat source alters the effective heat input and cooling rates to control the grain structure and phases. Selection of the controlling
parameters of these external sources, such as the frequency and amplitude of the ultrasound, is done by experimental trial-and-error. There is a need to develop mechanistic models of AM processes with external agitations to predict the desired parameters without time-consuming and expensive trials.

Process parameters are adjusted during printing [654–663] to achieve the desired microstructure and reduce defects. Generally, a closed-loop feedback system is used that analyses the data captured by sensors during the process and provides feedback to the controller to adjust the processing conditions in real-time. Fig. 9.18 provides an example of where this method was used to control the microstructure during DED-L [654]. A real-time closed-loop control process was developed and used to control the microstructure. An infrared-based thermal imaging system was developed to monitor the thermal process in real time. The developed system was capable of capturing the real-time cooling rate and melt pool temperature. The solidified grain structures were correlated with in situ thermal measurements to identify the appropriate procedure to control the microstructure. A closed-loop controller was developed and used to control the cooling rate in real-time. This method requires the setting up of additional accessories and sensors which may not be possible for all AM machines and require a high level of expertise.

10. Research needs

This review cites many examples where the current generally accepted understanding of microstructure and properties has been challenged [664], new alloys and applications are explored [665], and mechanisms are investigated for achieving the exciting combination of properties of metallic materials never before believed to be possible [145]. There are several variants of metal printing and each is affected by many process variables such as heat source power, scanning speed, deposition rate, and other variables that vary widely depending on the printing process and the alloy being printed [666]. Consequently, the parameter space window is large in additive manufacturing in comparison with more mature manufacturing processes such as welding and casting. Because of the complexities of the AM processes, more work is needed for the achievement of a significantly better understanding of the relation between the processing, microstructure, properties, and performance. The following are some of the focus areas to maintain and enhance the pace of progress.

10.1. Microstructural features that overcome strength-ductility trade-off

The microstructure of many commonly used alloys such as stainless steels, titanium alloys, and high-strength aluminum alloys contains multiple phases and precipitates in different length scales [3]. The microstructure is characterized by various phases, solidification structures containing cellular, dendritic morphologies, precipitates, and various defects that range in size from nano to mesoscale, and compositional variations owing to segregation and loss of alloying elements [3]. The various constituents in the microstructure vary in size by a factor of more than a million and the resulting heterogeneous hierarchical microstructures strongly influence the mechanical properties of the parts. Like in welding and casting, the phase transformations are strongly influenced by the thermal cycles, except there are multiple thermal cycles in additive manufacturing. Tempering of the phases during additive manufacturing during progressive deposition of layers of metallic materials occurs depending on the local heat transfer conditions that vary with the location within the part and time [180]. Moreover, the heating and cooling rates can be much more intense in additive manufacturing than in welding and casting. The resulting extensive variations of phase compositions, solidification microstructures, and defects such as dislocations have resulted in combinations of properties not attainable by other manufacturing processes. Examples include the simultaneous improvements of both strength and ductility in many cases, thus defying the commonly accepted norm of strength-ductility tradeoff where an increase in strength is commonly accompanied by a decrease in ductility [145,664]. While the hierarchical microstructure and the solidification morphology have been cited for the unique combination of properties, more work is needed for uncovering the mechanisms so that microstructures can be routinely tailored to achieve improved performance of parts.

10.2. Solidification morphology control

The solidification morphology depends on the ratio of the local temperature gradient, G, and the solidification growth rate, R [617]. These two parameters are dependent on a variety of factors that determine the local heat transfer condition, feedstock properties, and process variables. The cooling rates vary by five orders of magnitude depending on the linear heat input, which is the ratio of heat source power to the scanning speed [666]. The diversity in spatial and temporal variations of G and R and repeated thermal cycles present an unusual challenge for understanding the evolution of the solidification structure of printed metals. Many of the previous studies of morphology control originated from the lessons from casting and welding. For example, the addition of nucleants is commonly practiced in the foundry to achieve an equiaxed structure [667]. By adopting this time-tested practice, zirconia nanoparticles have been added to break up the growth of columnar dendrites to an equiaxed structure to prevent solidification cracking in printed aluminum alloy parts [104]. However, there is no direct way to predict the number of nucleation sites obtained by adding a certain amount of nucleant. In addition, the type of the nucleant, its size, and the amount are determined by trial and error and alternatives are being explored to achieve equiaxed morphology. One such method is the use of ultrasonic energy to break up the columnar grains [273]. The strength of the iron and aluminum alloy parts has also been attributed to the cellular structures. Although morphology control has been practiced in welding and casting for a long time, the implementation of the lessons to achieve equiaxed grains by adding expensive inoculants or applying ultrasonic energy to improve 3D printed parts needs more work.
10.3. Texture

Since texture affects the mechanical properties of additively manufactured parts, particularly the yield strength and fatigue properties, it is important to seek a better understanding of the evolution of texture in AM samples. The heat source power, scanning speed, hatch spacing, and scanning pattern all play a part in influencing texture. In solidified alloys, the texture is aligned to the heat flow direction [156], and grains tend to continue from layer to layer along the heat flow direction. In thin parts, the heat flow direction is often towards the base plate and the solidification texture in cubic materials is parallel to the build direction [156]. Textured microstructure often results in anisotropy in properties that can affect mechanical performance in multi-axial loading. The effect of anisotropy on mechanical properties is not well understood and more work needs to be done [149].

10.4. Defects and their impact on properties

Defects in microstructures are present in different length scales and can affect mechanical properties. For example, the lack of fusion voids adversely affect tensile properties [157]. High thermal stresses may result in distortions and, in extreme cases, may result in delamination and adversely affect fatigue properties. Surface roughness may act as the source of stress concentration that may result in crack initiation under stress [668]. The role that different defects play in crystal plasticity, fracture, and fatigue are also affected by dislocations and other defects in the microstructure. In addition, different types of defects interact with each other and affect mechanical properties in a manner not clearly understood. A better understanding of the evolution of various types of defects and their role in affecting mechanical properties needs more work.

10.5. Creating a printability database

Undesirable microstructural components such as brittle phases and common defects can be largely avoided by an appropriate selection of alloys and process variables [3]. Progressive enrichment of a database that assimilates valuable information about the known susceptibilities of various alloys to defects and undesirable microstructural features will help practicing engineers avoid difficulties before alloys are printed [3]. Defects such as lack of fusion, cracking, surface roughness, porosity, residual stresses, and distortion originate from a combination of the alloy used, printing process, and process parameters [23]. A comprehensive assessment of the ability of a feedstock material to be printed as a sound part by a combination of a printing process and process variables is needed. Such a printability database [605] will help in the selection of an appropriate printing process-alloy combination and avoid poor microstructural features without expensive and time-consuming trial and error testing. The success of the weldability database for fusion welding indicates that a printability database will enable the research results in 3D printing usable in the industry.

10.6. Applications of the emerging digital tools

Additive manufacturing has been designed to use digital technology in production, monitoring, and process control [3]. Validated mechanistic models and machine learning algorithms can reliably predict microstructural features and they have the potential to effectively control and improve the microstructures of parts [1]. The mechanistic models calculate important parameters such as temperature fields, build geometry, and cooling rates from process conditions and thermophysical properties of the alloy. These data are then used in a microstructure model to relate processing conditions and alloy composition with important microstructural features such as phase composition, grain structure and topology, and precipitates [1]. Since the microstructural features are highly sensitive to alloy composition, printing techniques, and process parameters, predictions of these characteristics using verifiable mechanistic models before printing are helpful for their control. However, in many cases, mechanistic information is not available and data-driven machine learning codes can provide quantitative correlation between microstructural features, the processing conditions, and alloy composition [1]. A case in point is the formation of cracking in many aluminum and nickel alloys that occurs via multiple mechanisms [105,669]. In the absence of definitive mechanistic understanding, machine learning codes use data and process conditions without phenomenological understanding to predict the evolution of microstructural features and defects. These algorithms can augment human intelligence based on experience to provide optimization of process variables and product attributes [1].

11. Outlook

11.1. Effect of process parameters on microstructure, grain structure, and texture

Only a handful of the over 5000 alloys have been investigated so far to understand the special features of AM that have a beneficial impact on properties [1]. In addition, new alloys are being developed specifically for additive manufacturing processes to take advantage of their unique features such as multiple thermal cycles to obtain superior properties [665]. Printing of silicon-containing steels [165] to achieve specific crystallographic texture for use in electric motors and transformers or affordable iron alloys containing nickel and cobalt [3] for applications where low thermal expansion coefficients are needed are examples of potentially attractive applications of new alloys with unique microstructures. Small changes in the microstructures of the existing alloys by taking advantage of the rich knowledge base of casting and welding may solve some of the persistent problems in AM [1]. For example, it has been known for a long time that certain additives in high-strength aluminum alloys promote the growth of equiaxed grains and prevent solidification cracking [105]. Developing a comprehensive knowledge base for understanding microstructural features and how they
are related to multiple properties is contributing to the printability database where the alloy-process combinations can be examined for their suitability to print sound components [605]. Apart from revealing the outcome of process-materials combinations, they will also continue to enrich the fundamentals of phase transformations, elemental segregation, formation of metastable phases, grain and sub-grain structures, and defects in mesoscale to as small as the crystal defects that result in unique properties during AM.

11.2. Improved understanding of the unique combination of properties

The serviceability of parts depends on a combination of several properties. Optimizing process combinations to achieve the desired combination of properties will undoubtedly result in a unique combination of properties never before thought possible [3]. Overcoming the strength-ductility tradeoff is a case in point. In most cases, an increase in the strength of alloys is accompanied by a decrease in ductility. However, in certain stainless steel and other alloys, this common paradigm has been overcome and simultaneous improvements in either one or both of the properties have been achieved [145,664]. As we study the underlying mechanisms, the new knowledge will undoubtedly lead to better properties and serviceability of parts.

11.3. New alloys

The crystal structures of the iron, aluminum, nickel, and titanium-based alloys are determined by both the unit cells of the solvent atoms modified by the solutes they contain. Additions of the nature and amount of solutes have been the basis to control the solidification behavior, grain morphology, phase compositions, and mechanical properties of the alloys [1]. However, the microstructures of metallic materials are notoriously sensitive to external impulses such as cooling rates and stresses [3]. The existing iron, aluminum, nickel, and titanium-based alloys that are used in AM were not designed specifically for additive manufacturing [3]. Most variants of additive manufacturing involve multiple thermal cycles that affect the microstructure and properties of metallic parts. Process models that can predict thermal cycles are emerging [1]. However, it is anticipated that relating process variables with microstructure and properties of parts is a slow process because of the large number of process variables, their wide range, and the alloy-specific nature of microstructure and properties [666]. Advanced modeling can assist in controlling thermal cycles that are useful for insight into the evolution of microstructure. In addition, the development of new alloys and functionally graded materials will continue [665] that when exposed to the AM conditions can result in microstructures and properties that will meet the performance needs of the parts for qualification.

11.4. Fewer defects

Lack of fusion defects, cracking, residual stresses and distortion, various types of porosity, surface roughness, waviness, balling, and change in microstructure and crystal defects such as dislocations are important microstructural features of additively manufactured parts [23]. Multiple defects in mesoscale and smaller, all the way to the atomic scale profoundly affect the properties and serviceability of parts. Post-processing such as heat treatments and hot isostatic pressing will continue to be used to mitigate defects such as porosity, lack of fusion, and residual stresses but these steps compromise the cost competitiveness of parts, and progress is being made to mitigate defects [3]. Defects in all scales also play a part in affecting mechanical properties in a complex manner. Although significant progress has been made recently to quantitatively understand the origin of the defects and the hierarchical influence of various process variables, at present, there is a scarcity of quantitative frameworks for understanding the correlation between the process variables with the defects and mechanical properties of parts. Continuing progress in the applications of mechanistic modeling and machine learning has the potential to narrow down the process parameter window to control defects and improve the serviceability of parts [1].

11.5. Improved integration of digital tools

There are many examples of how important parameters which affect product quality such as the temperature and velocity fields, cooling rates, solidification morphology, and the scale of microstructure can be computed using verifiable mechanistic models [1]. These parameters are difficult to measure experimentally because of the small size of the fusion zone and the strong spatially variable, transient nature of the temperature field. When mechanistic models are combined with experimental data [1], the scientific basis for the understanding of the evolution of microstructure and properties can be uncovered. As the benefits of the use of mechanistic models are more widely appreciated, the selection of parameters for the printing of sound parts will be guided by scientific principles thus avoiding time-consuming and expensive trial and error [1].

Machine learning is a natural fit for additive manufacturing because of its origin in digital technology. From product design to process planning, to production monitoring and control to connecting process variables to product attributes, machine learning will serve a more important role than its current usage [1]. An integrated data collection system by a vision system can gather data during the printing of each layer and machine learning can use the temperature fields and materials states to reduce production errors. Control of microstructure and properties are perhaps the most important features that will be impacted by machine learning because currently there is no reliable way to predict complex properties of metallic materials from phenomenological understanding [105]. Microstructures of additively manufactured metallic materials are complex because of the diversity of phases, grain and sub-grain structures, segregated elements, metastable phases, very fine oxides and other precipitates, and high concentrations of dislocations near grain boundaries. These diverse features of the microstructures make the correlation between the microstructure and properties complex.
Machine learning when the quality and volume requirements of data are met and appropriate precautions are exercised for the prediction errors provides a potential alternative to correlate microstructure with multiple properties and improve the serviceability of parts based on scientific principles [1,105].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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