Microstructural Control of Additively Manufactured Metallic Materials

P.C. Collins,¹,²,∗ D.A. Brice,¹ P. Samimi,¹ I. Ghamarian,¹ and H.L. Fraser³

¹Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011; email: pcollins@iastate.edu
²Ames Laboratory, Iowa State University, Ames, Iowa 50011
³Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio 43210

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Abstract
In additively manufactured (AM) metallic materials, the fundamental interrelationships that exist between composition, processing, and microstructure govern these materials’ properties and potential improvements or reductions in performance. For example, by using AM, it is possible to achieve highly desirable microstructural features (e.g., highly refined precipitates) that could not otherwise be achieved by using conventional approaches. Simultaneously, opportunities exist to manage macro-level microstructural characteristics such as residual stress, porosity, and texture, the last of which might be desirable. To predictably realize optimal microstructures, it is necessary to establish a framework that integrates processing variables, alloy composition, and the resulting microstructure. Although such a framework is largely lacking for AM metallic materials, the basic scientific components of the framework exist in literature. This review considers these key components and presents them in a manner that highlights key interdependencies that would form an integrated framework to engineer microstructures using AM.
1. INTRODUCTION

The microstructures that are produced by additive manufacturing (AM) are complex, often varying spatially within a build. The complex thermal histories that are associated with AM processes strongly influence the microstructure, as each discrete volume of a component deposited by an AM technique may have a thermal history that differs significantly relative to the adjacent volume (e.g., near edges). Furthermore, the breadth of AM processes results in profoundly different thermal histories and thus profoundly different microstructures. To understand the significant variation that can occur, and the differences relative to conventionally processed materials, it is necessary to understand how microstructure evolves in AM materials.

First, it is necessary to appreciate the diversity of AM processes and the breadth of material classes that can be processed by AM, which has increased markedly over the past decade (1–4). For the purposes of this review, the focus is AM processes that are used to produce bulk metallic articles. The generic AM process may be defined as a process in which a local heat source melts both a small volume of the supporting architecture (e.g., substrate or previously deposited material) and an additional volume of new material while the heat source is in constant motion relative to the supporting architecture and newly deposited additional material (see Figure 1). This definition satisfactorily captures all heat sources (laser, electron beam, plasma), all feedstock (powder bed, powder blown, wire fed), and all systems independent of the reference frame for motion (heat source versus part versus coupled motion). AM systems are further defined by the atmosphere in which the melting and solidification are occurring, which may be vacuum, inert gas, gas shield or shroud, or air. Although these details, which influence the microstructures, vary considerably among the different AM technologies, AM is essentially a highly localized solidification process whose resulting microstructure is governed by heat transfer, phase transformations, and the thermophysical properties of the constituent elements and phases. This review article cannot cover all aspects of the process parameters. Consequently, the article focuses on the energy input and does not consider how input feedstock (e.g., powder morphology, particle size distributions)}
INFLUENCE OF METAL POWDER CHARACTERISTICS ON MICROSTRUCTURES IN ADDITIVELY MANUFACTURED COMPONENTS

Generally, the simulation of microstructural evolution assumes an input energy sufficient to melt all incoming material. As described in Section 2.1, the required input energy is a function of various thermophysical properties, including the enthalpy of fusion. For powder-based approaches, this required energy represents a minimum energy and does not include any variation in the spatial and temporal addition of the incoming powder or its size distribution, morphology, or surface characteristics. For powder-blown approaches, recent efforts have focused on the attenuation of the incident power as a function of the spatial distribution of the powder (126, 127), but much work remains to be done to predict the powder interactions in the liquid pool, especially when the local degree of superheat is low (e.g., near the moving solid/liquid interface) near the splash zone. In powder bed approaches, the powder size distribution, morphology, and surface characteristics influence the power absorption in a spatial manner. Although there exist efforts to predict the evolution of material in both powder bed and powder-blown approaches, the influence of powder characteristics remains an underexplored aspect of the simulations. Much effort is needed to characterize the powder and to incorporate precise measurements into simulations.

Influences the process or resulting microstructure. For additional details regarding the current level of understanding of the interrelationship between powder attributes, process parameters, and the resulting microstructure, please see the sidebar entitled “Influence of Metal Powder Characteristics on Microstructures in Additively Manufactured Components.”

There are commendable efforts under way to model and predict the heat transfer associated with AM, which is a dynamic and coupled problem characterized by a spatially and temporally varying heat source and part geometry (5–9). In addition, there are modeling efforts under way to understand and capture the physics operating in the molten pool (10–12). Such modeling efforts are referenced where illustrative and informative. However, this review article primarily frames the referenced research on the basis of understanding gained in the areas of (a) melting, solidification, and the attending phenomena; (b) the thermodynamics of the process and reactions, including both \( L \rightarrow S \) and \( S \rightarrow S' \) phase transformations; and (c) the effect that composition and processing have on the attending microstructure.

Given the hierarchical nature of microstructure of most structural and functional metallic materials, this article is organized according to the characteristic length scales and includes macro-level features that are morphological [microstructural (in)homogeneities], micromechanical (residual stress), and crystallographic (texture); micro-level features such as details of grains (size, morphology) and phases (scale, distribution, volume fraction, morphology); and compositional features such as chemical partitioning, volatilization, and interstitial gettering. Where possible, the advances in modeling are presented. In addition, a framework to illustrate the various composition, microstructure, and property linkages is presented. Finally, it is important to directly describe the opportunities and limitations for AM materials as they relate to microstructure.

2. MACRO-LEVEL MICROSTRUCTURAL FEATURES

2.1. Material and Microstructural Discontinuities

As Figure 2 illustrates, for AM materials, the material discontinuities include porosity, unmelted or partially melted particles (Figure 2a), delamination between adjacent passes or previous layers,
Examples of insufficient energy (porosity and lack of fusion) Examples of excess energy (balling and hot tears) Examples of fish scaling

and lack of fusion with previously deposited layers or passes (Figure 2b). These features invariably impact mechanical properties such as measures of uniaxial tension ductility, fracture toughness, and fatigue. Most AM research emphasizes intrinsic near-net shape advantages, which correspondingly deemphasizes (i.e., ignores) any deformation-based processes subsequent to solidification (13) such as forging, rolling, and extrusion. Any material discontinuity that is created during the AM process is likely to be persistent without a postprocessing step such as hot isostatic pressing. In most applications, eliminating these material discontinuities is desirable. There are notable exceptions, including, for example, biomaterials, in which engineered porosity levels or channels may be desirable (14, 15). In both cases, it is necessary to understand the relationship between processing parameters and the resulting presence and distribution of porosity or unmelted/partially melted particles. This relationship relates to both input power and feedstock, for which there is a dearth of information in the literature.

Many researchers have adopted approaches by which they combine process variables (e.g., spacing between adjacent passes, input energy, travel speed) or melt pool geometry to calculate an energy density factor (16–21). Such energy density factors can then be related directly to the volume fraction of porosity or indirectly to volume fraction material discontinuities by assessing ductility for a given material as a function of the energy density factor. At a certain minimum energy density (i.e., the critical energy density), the ductility or reduction in area reaches a plateau, indicating a minimum fraction of pores or unmelted particles. The critical energy density is a function of the material system. More fundamentally, the critical energy density is related to the efficiency by which the input energy is absorbed by the material in the presence of power losses (e.g., reflectivity, vapor plumes, electron and photon scattering) and enthalpies of fusion. Low energy densities result in low superheats in the molten pool and limit convection, leading to inhomogeneous mixing (22) and to the formation of certain types of porosity or incomplete melting of powder (18, 21, 23–26). For elemental powder blends, the critical energy density
depends on the thermophysical properties of the constituent elements and on the thermodynamic
interactions between the constituent elements (23, 24). In short, a minimum energy is required
to fully melt the volume of material of importance to the process. In theory, there should also be
a maximum energy density, which would be defined by volatilization of constituents at very high
superheats. The volatilization of elements has been suggested to be associated with near-spherical
defects (27), whereas the destabilization of the liquid interface can lead to balling (Figure 2c)
and to undesired trapped, spherical particles (28–30). Although these energy density approaches
provide a useful rule of thumb, they neglect the microscopic details of the melt pool physics,
including convective flow, temperature gradients, and the stochastic nature of certain phenomena
[e.g., powder position in powder bed or powder-blown AM processes (31) and keyhole collapse
in electron beam processes (32)]. Modern modeling approaches (10, 13, 33) are able to provide
greater understanding of some of these microscopic details and are quite useful. Nonetheless,
most models lack certain aspects of the melt pool physics, including the stochastic nature of the
feed material and operating physics, which are difficult to model (34).

The above discussion excludes layer delamination and lack of fusion with previously deposited
layers or passes. Both types of material discontinuities have been observed in multiple studies but
have largely been neglected in the literature. Regarding layer delamination, there are multiple
possible origins, including thermal expansion or contraction and the unexpected formation of
surface oxides. Delamination is a residual stress–mediated process (35). In addition, hot tearing,
which is a function of the material response to stress at elevated temperatures, can occur in some
materials (Figure 2d). Regarding lack of fusion, there are two likely causes. The first is operating
at low energy densities, at which the size of the molten pool is smaller than the adjacent passes of
the tool path (13). The second is operating at high energy densities and is likely due to unexpected
thermal distortion of the part, separating the local expected supporting architecture from the
coupled heat source and new feed material.

In addition to these material discontinuities, there exists a microstructural discontinuity: the
so-called fish-scale feature (22, 36, 37) (Figure 2e,f). This feature may appear due to variations
in solute concentrations that likely occur during solidification, variations in precipitate formation,
and variations in precipitate morphology.

2.2. Residual Stress

The highly localized heat source, its motion, and the relatively slow heat conduction induce
large thermal gradients ($G = |\nabla T|$) in AM materials. Although these thermal gradients directly
influence the microstructure of AM materials by governing texture and grain morphology, as is
shown in subsequent sections, such gradients also promote residual stresses that can be quite large
(38) and that can lead to distortion of the components and unexpected changes in the mechanical
properties.

Residual stress is included as a hidden, and often neglected, microstructural variable for the
purposes of this review. The AM process parameters, thermophysical properties of the material,
geometry and shape of the part, and operating heat transfer mechanisms govern the magnitude
and shape of the residual stress field (35). Briefly, residual stresses are established when the material
expands upon heating or melting and contracts upon cooling. The cyclic expansion or contraction
of each new surface establishes a residual tensile stress state at the top of each layer, which is
surrounded by a compressive stress state (see Figure 3a). A few leading researchers, including
Mercelis & Kruth (39) and Michaleris and collaborators (5, 6, 38), have predicted residual stress in
various types of AM. In their papers, their simulations indicate that the residual stress varies across
a layer and predict that the tensile stresses at the top and bottom of a layer are greater in magnitude
than the compressive stresses that develop. Other authors have quantified the magnitude of residual stress in various systems, showing that such residual stress can be quite high (\(\sim 400–800\) MPa) in Ni-based superalloys (38, 40), lower (\(\sim 100–200\) MPa) in Ti-based alloys (38) (see Figure 3c), and lower still (\(\sim 25\) MPa) in Al-based alloys (41) (unless otherwise specified, all compositions in this review are expressed in weight percent). The complex residual stress field ranges from compressive to tensile, depending upon location (38, 41) (see Figure 3b). Importantly, the degree of residual stress is related to the energy density. Sochalski-Kolbus et al. (37) compared two AM methods with a significant difference in the energy density for a Ni-based superalloy (Inconel 718). The resulting residual stress (135 MPa) in the system with the higher energy density was much higher than the residual stress (21 MPa) of the other system. Roberts et al. (42) showed that the residual stress that develops in a material is directly related to the thermal gradient in the melt pool, which increases with increasing energy density. These efforts demonstrate that the residual stress can be controlled by the thermal gradients. Many authors propose strategies based upon modifying the relative motion of the heat source or intermediate anneals to help control the residual stress.

Importantly, the existence of the residual stress during deposition (i.e., while the component is at
a significant fraction of its melting point) can result in distortion (see Figure 3d), microcracking, or hot tearing, especially in Ni- and Fe-based alloys (35), leading to another type of material or microstructural discontinuity.

Most of the ongoing research efforts to understand and predict residual stresses in AM materials focus primarily on large, macro-level residual stresses [i.e., type I residual stresses (43, 44)]. However, the subsequent phase transformations result in additional (type II) residual stresses that may need to be considered in the future.

2.3. Texture

Figure 4a shows a schematic of the solidification process adapted from Bermingham et al. (45) and includes details associated with the thermal gradients and various physical processes, including vaporization, convection, power losses, and solidification. AM is fundamentally a highly localized solidification process. Consequently, coarse macroscale microstructural features such as texture and grain morphology may be understood concurrently using theories typically associated with solidification.

A large number of researchers have reported texture in their as-deposited AM material across a wide range of alloys, including Ti-based alloys (45–48), Ni-based alloys (49–51), Al-based high-entropy alloys (HEAs) of both bcc and fcc types (52), and others (53). Each of these materials solidifies first as a cubic structure (Ti as bcc β, Ni as fcc γ, and Al HEAs as either bcc or fcc), and each adopts a <001> fiber solidification texture (see Figure 4c). Importantly, these textures tend to be directly correlated with high-aspect-ratio grains that are continuous across multiple layers (see Figure 4c) and are related to the primary solidification growth directions. These results are fully consistent with the growth of both cellular and dendritic structures, as presented in the work of Chalmers (54), Morris & Winegard (55), and others (56, 57). In the classical treatment of solidification, a <001> fiber solidification growth direction was reported to be parallel to the maximum thermal gradient for most cubic systems. Liu et al. (58) have demonstrated that this <001> growth depends on the anisotropy of the solid-liquid interfacial free energy \( \gamma_{SL}(\hat{n}) \) and interfacial stiffness \( \gamma_{SL}(\hat{n}) / \Delta \gamma_{SL} \) for different planes. The reduced tip radius of the fastest-moving interface (e.g., the tip of a cell or dendrite) has an undercooling (\( \Delta T_c = K \gamma \)) driven by the radius of curvature (\( K = 2/r \) for a sphere), where \( K \) is the Gibbs-Thompson term. Here \( \gamma_{in} \) is the molar volume of the solid, \( \gamma_{SL}(\hat{n}) \) is the interfacial free energy including stiffness, and \( \Delta S_f \) is the entropy of fusion. Given the anisotropic nature of the free energy and stiffness contributions to texture, it is possible to modify the growth texture away from <001> for cubic systems. For example, a <110> texture has been demonstrated in Al alloys (59) by small additions of Zn, Mg, and Ti (60, 61). Such a <110> texture has been related to observations of so-called feathery dendrites in castings but has largely been unexplored in AM systems. Nonetheless, such demonstrations confirm the possibility of gaining a fundamental understanding of what controls texture and thereby the possibility of modifying texture through changes in alloy composition.

Two other observations drawn from the literature are important to consider. First, although many researchers cite the <001> fiber growth direction as being parallel to the \( z \)-axis, there can often be subtle deviations (of up to \( \sim 10–20^\circ \)) from the \( z \)-direction, which is reflected in either the graphical representations of texture (e.g., pole figures) or assessments of the long axis of the grains that formed during solidification. This deviation in the crystallographic texture can be attributed to the fact that the maximum temperature gradient is not parallel to the \( z \)-axis. When the complex temperature distributions of AM (captured by Equation 1) and the motion of the heat source relative to the solid material that acts as a chill are considered, it becomes clear that AM deviates from a simple 1D heat transfer problem and that the maximum temperature gradient is not parallel
Increasing constitutional supercooling

\[ \Delta T = \alpha \nabla^2 T = \left( \frac{k}{\rho c_p} \right) \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right), \]

where \( \alpha \) is the thermal diffusivity (\( \alpha = k / \rho c_p \)), \( k \) is the thermal conductivity, \( \rho \) is the density, \( c_p \) is specific heat capacity, \( T \) is temperature, and \( t \) is time.

Second, under certain combinations of thermal gradients and processing conditions (62, 63) and for certain alloy modifications (47), texture can apparently be controlled or eliminated in

to a principal Cartesian coordinate axis (\( x \), \( y \), and \( z \)). It is understood that the complex thermal field can be included in the thermal modeling of AM solidification,
the as-deposited state. Regarding the former, the transition between textured (columnar) and non-textured (equiaxed) structures has been related to spatial-temporal variation in the thermal gradient \( G = |\nabla T| \) and the solidification rate velocity \( R = \frac{1}{\eta} \frac{\partial T}{\partial t} \), where \( \frac{\partial T}{\partial t} \) is the solidification cooling rate \( (62–65) \). These terms, and their contribution to the microstructure (see Figure 4b), relate to constitutional supercooling, which influences not only texture but also grain structures.

One strategy of predicting the dominant morphology, and consequently the presence or absence of texture, is the use of \( G \)-versus-\( R \) maps, also known as solidification maps \( (64–67) \) (see Figure 4b, d). These \( G \)-versus-\( R \) maps are strongly dependent upon composition, as the phenomena (e.g., constitutional supercooling, crystal anisotropy) that govern liquid/solid interfacial instabilities are dependent upon composition (e.g., partition coefficients, diffusivity in the liquid) \((45)\). Thus, another approach that could be adopted is the use of \( G/V \)-versus-\( X \) maps \((59, 68, 69)\).

In addition, cellular automaton modeling is a suitable method of predicting both grain structures \((70, 71)\) and the evolution of texture.

It is also useful to consider the persistence of texture following postdeposition heat treatments and as a result of phase transformations. Regarding the former, it is widely reported that the texture generally remains following postdeposition, elevated-temperature heat treatments \((46)\), especially when care is taken to consider the columnar-to-equiaxed transitions (CETs) that exist in the as-deposited material. This retention of texture is not unexpected, given the lack of a sufficient driving force for nucleation of new grains. For materials that undergo a phase transformation upon cooling, the texture propagates from the high-temperature phase to the low-temperature phase, following the governing orientation relationships \((72, 73)\). The texture that is present in AM materials can either negatively affect properties [e.g., reduced ductility in Ti-6Al-4V \((74)\)] or positively affect properties [e.g., enhanced ductility in a Co-Cr-Mo alloy \((53, 75)\)], although the precise impact on properties, including fracture toughness and fatigue, can be understood only when the role of defects and other microstructural details is also considered. This is a coupled problem and requires an understanding of the correlation between texture and defects.

3. MICRO-LEVEL MICROSTRUCTURAL FEATURES

3.1. Grain Size and Morphology

The coarsest microstructural features that are typically important to consider are the grains. There are direct linkages between texture and solidification maps, which are introduced in Section 2.3 above, and grain size and morphology. Several distinctive characteristics regarding grains have been observed in AM metallic materials. These characteristics include (a) a zigzag-like appearance to columnar grains across alternating layers \((18, 72)\), (b) an ability to control grain size or shape by varying processing parameters \((67)\), (c) an apparent ability to undergo a CET by modifying composition \((45, 76–78)\), and (d) periodic CETs \((62, 79, 80)\). These features can be understood by considering the solidification process. Many of the grain characteristics observed in AM can be understood by using Figure 5, which extends concepts introduced in Figure 4.

Significantly, although an overarching definition of AM is presented in the introduction, there are differences in the operation of various mechanisms of heat transfer (i.e., their operation and magnitude) for different AM techniques. For example, heat conduction dominates electron beam-based AM, whereas convection operates in laser-based AM under Ar. Furthermore, heat transfer by conduction is different for a powder-blown thin wall (approximates a 1D problem), whereas it is more complex in a powder bed thin wall, for which heat transfer through percolation theory is present. As the dimensionality of the part increases to larger 3D volumes, such differences between powder bed and powder blown may be reduced, although differences in the input power...
Figure 5
Effect of processing on texture and grains in AM. (a) Schematic of molten pool motion on successive layers promoting a zigzag pattern. The molten pool is designated and shaded in orange, whereas the solid metal exhibits multiple grains defined by their boundaries (blue dotted lines). Redrawn from Reference 129. (b) Observed zigzag patterns. Adapted from Reference 18. (c) Texture differences in the titanium alloy TNZT (Ti-35Nb-7Zr-5Ta) (adapted from Reference 76) and TNZT + B (Ti-35Nb-7Zr-5Ta+2B) (adapted from Reference 77). (d) Columnar-to-equiaxed transitions (CETs) observed in the literature. Adapted from References 62 and 79.

Abbreviations: CGZ, coarse grain zone; EGZ, equiaxed grain zone; HAZ, heat-affected zone; RD, rolling direction; TD, transverse direction.

(q) and travel speed must still be considered. These processing subtleties are expected to modify significantly the thermal gradients of the systems and thus the size and morphology of the grains.

Figure 5a describes a phenomenon that can best be described as a ∇T-induced grain morphology. Here, two successive laser passes (i.e., n and n + 1) are schematically illustrated. The motion of the beam (v) induces a maximum thermal gradient (G = |∇T|) that deviates from the z-axis. If the grains grow in a planar, cellular, or columnar manner from the cooler solid, their long
axis tends to align with the maximum thermal gradient. Thus, when these two alternating layers are considered, their maximum thermal gradients should alternate by approximately the same angular deviation about the z-axis, thus potentially inducing a zigzag grain pattern. Such grains have been observed by multiple researchers, including Thijs et al. (18), whose work is shown in the optical micrograph in Figure 5b. Grains such as those discussed in the work of Thijs et al. (see Figure 5b) are likely new nucleation events whose solidification front behaves in a cellular or dendritic fashion, as opposed to grain continuation (e.g., via epitaxial growth), as such a deviation in the primary axis would induce considerable lattice curvature in the grains at the layer-layer boundary. Given that both epitaxial growth and new nucleation zigzag patterns have been observed, one must consider that the thermal gradient term might be further probed to understand the change in modes. This area has not been addressed in the AM literature.

Figure 4c shows that differences in undercooling change the mode of solidification (e.g., planar, cellular, columnar dendritic, equiaxed dendritic), which is the basis for the solidification maps shown in Figure 4c,d. The compositional regime for which constitutional undercooling is favorable can be related to two descriptive parameters, namely the supercooling parameter $P$ and the growth restriction factor $Q$, where $P = mc_0(k-1)/k$ and $Q = mc_0(k-1)$, respectively (78, 81–84). Here, $m$ is the slope of the liquidus line, and $k$ is the partition coefficient. $P$ represents the degree of constitutional supercooling present, whereas $Q$ represents the rate of development of the constitutional supercooling. When constitutional supercooling is increased (i.e., given favorable $P$ and $Q$) and as the thermal gradient decreases, an increasingly greater constitutional supercooling can occur, leading to the change in solidification mode. This is illustrated for an arbitrary alloy with a narrow freezing range and a simple linear thermal gradient. For each solidification mode, the vertical axis is the temperature, and the horizontal direction is the distance from the liquid/solid interface. By using this common schematic representation of the influence of undercooling on solidification modes, it is possible to understand how the mode might change if the temperature gradient ($G$) was changed. Such a change in solidification modes is indeed the basis for the solidification maps presented by Kobryn & Semiatin (67) shown in Figure 4d and similar process maps (85) and is used to understand the evolution of grain structures in Ti-6Al-4V by using markedly different processing routes (e.g., 14-kW CO$_2$ lasers and 750-W Nd:YAG lasers).

There are other means of modifying the solidification mode and the attending grain morphology. One such way is to increase the freezing range (i.e., by increasing $P$ and decreasing $Q$). A model system in which this approach has been demonstrated is Ti-based alloys with and without boron (B). Bermingham et al. (45) effectively demonstrated this approach by modifying Ti-6Al-4V with trace B. They observed the direct influence of $Q$ in promoting thinner $\beta$-grains but were unable to transition this alloy to a more equiaxed dendritic structure. However, two separate investigations of a $\beta$-Ti alloy, TNZT (nominally Ti-35Nb-7Zr-5Ta), with and without B, show the ability to significantly reduce grain size and texture, indicating a more equiaxed dendritic structure. In the first study of laser-deposited, unmodified TNZT by Banerjee et al. (76), an electron backscattered diffraction pattern (EBSP) map (shown in Figure 5c) indicates a very strong (～26-times-random) [001]$_\beta$ fiber texture with a grain size of ～150 μm. The second study by Nag et al. (77) focused on the characterization of the borides in TNZT + 2-wt% B, rather than on the effect of B on the grains. Nonetheless, the research, conducted using the same AM system, presented an EBSP map (also shown in Figure 5c) in which the grains not only deviate from the [001]$_\beta$ fiber texture but seem far more random and of a significantly reduced size (～5–10 μm) than those in the study of Banerjee et al. (76). Although the precipitation of thermally stable borides as inoculants likely also reduced the grain size, the role of constitutional supercooling and $Q$ cannot be ignored in these two separate studies. Another system in which composition has induced considerable grain size reduction is a Ti alloy with a relatively large carbon (C) content, designated as BurTi (86, 87).
When C is added to the alloy, there is a considerable reduction in grain size relative to alloys such as Ti-6Al-4V. C does not exhibit the same relatively high $Q$ as B, owing to its solubility in both $\alpha$- and $\beta$-Ti; consequently, it is not expected to restrict grain growth to the same degree. Thus, in the case of this alloy, the grain refinement might be attributed more to the precipitation of thermally stable precipitates than to constitutional supercooling. Although these studies present compelling experimental results indicating that composition can play a role in disrupting texture, they generally [except for the work of Bermingham et al. (45)] have yet to consider the importance of solidification modes.

Another method by which to control the texture is to modify the thermal fields. By modifying the thermal fields, it is possible to transition across solidification modes in the solidification maps described previously. Dehoff et al. (88) recently demonstrated the ability to control solidification modes, and thus texture, by controlling the processing parameters. In their demonstration, they showed it was possible to engineer the texture in the $x$-$y$ plane of a deposition, effectively writing texture where they wanted it. Beyond this breakthrough effort, little else has been done. Yet there is an opportunity. As noted above, the temperature gradients are complex and vary among the AM methods. For those methods that are conducted in either atmosphere or powder bed, there are additional modes of heat transfer beyond simple conduction through the build, which will produce a complex, nonlinear temperature field. For such a field, it is not surprising if $\frac{d^2T}{dx^2} = 0$, reflecting a competition between two different thermal gradients, as illustrated in Figure 5d. Under such conditions, columnar grains can dominate the bottom part of the melt pool, whereas equiaxed grains dominate the top part of the melt pool (79). In such reports, for a multilayer AM build, a portion of the equiaxed grains of the previously deposited layer melts, and new nucleation may proceed by the columnar dendritic mode, whereas the top of the next layer also exhibits equiaxed grains. In this manner, it is possible to observe a repeating CET whose overall height is slightly less than the layer thickness, owing to remelting. CET has also been observed in high-energy-input wire-fed electron beam work that is dominated by only one heat transfer mode (conduction) (80). In such work, constitutional supercooling is likely responsible for the observation of CET, which is less pronounced than the CET shown in Figure 5d.

Panels a and b of Figure 6 show two examples of modeling strategies that have been used to predict grain structures in AM materials. As shown in Figure 6a, Yin & Felicelli (71) combined a 2D finite element modeling approach with the cellular automaton technique to predict the

![Figure 6](image)

**Figure 6**
Application of cellular automaton and finite element modeling simulation tools to predict microstructural evolution in metal AM. Panel a adapted from Reference 71. Panel b adapted from Reference 70.
evolution of grains; showed the transition from dendritic to cellular structures; and incorporated the influences of travel speed, layer spacing, and base plate thickness into the model. As shown in Figure 6b, Klingbeil et al. (70) used the cellular automaton approach to predict grain growth in AM Ti-6Al-4V and correlated the results of simulations with experiments.

3.2. Phases

Industrially relevant structural metals tend to be multicomponent and multiphase materials (e.g., Ni-based superalloys, precipitation-hardened Al alloys, and α+β- and β-Ti-based alloys), relying upon second phases to strengthen the material. In such multiphase materials, both the $L \rightarrow S$ and $S \rightarrow S'$ phase transformations are important. The former determines the distribution of elements within the grains, whereas the latter establishes the volume fraction, size, and distribution of second phases present in the microstructure.

The above sections establish that in the AM process there are often temperature gradients that result in far-from-equilibrium structures. The same large undercooling observed in AM materials that promotes texture and governs grains also impacts the resulting phases and their sizes, distributions, and chemical compositions. Compounding the evolution of microstructures in the as-deposited condition are the spatial and temporal fluctuations of temperature, which can result in the dissolution and reprecipitation of phases, but at different temperature gradients (see Equation 1) relative to the adjacent microstructure, leading to spatially varying microstructures.

Given that these are highly nonequilibrium and potentially nonuniform microstructures, it is useful to consider briefly the thermodynamics and kinetics associated with phase transformations, given some of the novel microstructures that may be achieved using AM. Figure 7 provides a framework that captures the types of possible phase transformations, as well as the influence of undercooling on the resultant phases. Consider first the left-hand side of the generic binary eutectoid phase diagram depicted in Figure 7a. In this region, $T_\alpha$ (which is the locus of all $x_\alpha$ for which $G_\alpha = G_\beta$ at various temperatures) is included, as is $T_\beta$, which has an identical meaning, but for the β phase. The $T_\alpha$ curves are the lower bounds to which a pure diffusional transformation can occur. Below these curves, partitionless phase transformations occur; the parent phase (here liquid) can transform to the product phase without a change in the composition. Depending upon the degree of undercooling, diffusion can still occur, as solute can pile up in front of a growing product phase; hence, partitionless phase transformations are not necessarily diffusionless. For a sufficient degree of undercooling, diffusionless phase transformations occur, in which the product phase exhibits the same composition as the parent phase (e.g., massive or martensitic transformations) and often involves the breaking of parent symmetry and a resultant metastable phase. Significantly, this same hierarchy can exist for solid/solid phase transformations, such as the formation of martensites in Fe- and Ti-based alloys, which are commonly observed by researchers in the literature.

It is useful to now consider both the $T_\alpha$ and $T_\beta$ curves. In the highly schematic eutectic phase diagram presented in Figure 7a, the $T_\alpha$ and $T_\beta$ curves plummet and are well separated with respect to composition. Under such conditions, bulk metallic glasses can form, as illustrated in Figure 7a. Some researchers, including Wu et al. (89), Sun & Flores (19, 90), and Yang et al. (91), have used different techniques to affect bulk metallic glasses using AM (19, 90) or laser surface glazing (89, 91). Such techniques are included here, as the principles are extendable to AM. If the $T_\alpha$ and $T_\beta$ curves were to intersect at a reasonable (elevated) temperature, then a fully eutectic microstructure could form in compositions away from the eutectic composition, as the proeutectic phase would not form prior to transformation.
This framework illustrates that, on the basis of composition and cooling, it is possible to form equilibrium phases, including both partitionless and diffusional transformations; metastable phases, including both martensitic and massive transformations; and bulk metallic glasses. Although this framework is introduced to understand phase transformations associated with far-from-equilibrium phases, it can be used to understand phase transformations expected under equilibrium conditions. For example, Figure 7b shows that, under conditions commonly found in AM, the compositions of the expected phases may be far from their equilibrium compositions. With increased undercooling, there is insufficient time for the solute to redistribute itself in front of the moving liquid/solid (or solid/solid) interface, and the relative compositional difference between the phases decreases as the partition coefficient (k) approaches 1. This is discussed further in Section 4. Finally, consider the connections between the variables associated with nucleation and growth, mapped out in Figure 7c. According to well-understood relationships in nucleation, as undercooling is increased, both the critical radius of a stable particle (r*) and the critical free energy to nucleation (∆G*) are reduced. It is useful to consider the role that partitioning has on r* and ∆G*, although such discussion is often neglected. The distribution of solute atoms changes the strain energy [∆G_{strain}] as well as the surface energy [γ_{α/β}(Θ)] of the particle. Significantly, AM results in strong texture, which is likely to introduce a heterogeneous distribution of grain boundaries that deviate from a fully random microstructure. To understand precipitation in AM systems, these deviations need to be considered.
As discussed above, many researchers have observed the proclivity of Ti-based alloys to exhibit martensitic microstructures (α’). These martensitic microstructures are the result of an S → S’ (β → α’) phase transformation. However, these metastable phases that are formed in one layer of the build can be partially or completely decomposed into stable phases due to the thermal cycling effect during melting and fusion of the subsequent layer or preheating of the powder (in the case of powder bed techniques). The degree of decomposition is a strong function of process heat input and is thus correlated with the factors that influence the solidification rate of the molten pool such as the energy density, layer thickness, and even geometry of the sample (92).

The degree of undercooling for both L → S and S → S’ phase transformations varies spatially within the part, which can lead to variations in both the partitioning coefficient and the subsequent phases. Such a variation in solute distribution and subsequent phase formation is usually observed in systems that undergo a complex phase transformation pathway, including both relatively high and low temperature transformations. Thus, in the regions of the build that experience higher cooling rates, a lower fraction for phases that are the product of high-temperature transformation is observed, as their transformation is suppressed due to rapid cooling. The above-mentioned phenomenon has been reported in a γ-Ti-based alloy in which the phase fraction of the α2 phase in the near-substrate region is almost five times larger than the average α2 phase fraction in the rest of the build. In this system, the α2 → α2 + γ transformation is expected upon cooling. However, owing to the relatively high cooling rates during the formation of initial layers on the substrate (93), the expected phase transformation is arrested, and the higher-temperature phase remains. Similarly, this difference in undercooling can result in different dominant morphologies, as has been observed in the variation in the size of α precipitates in Ti alloys (73, 94) (see Figure 8a–c), as well as in phase fractions in Ni-based superalloys (95) and Al-based alloys (96).

The starting composition and complex thermal histories help set the resulting microstructure. For Ni-based superalloys, some alloys [e.g., Inconel 718 by selective laser melting (SLM)] do not readily develop the γ’ phase from processing and require additional heat treatments to achieve the desired distribution of precipitates (97), whereas other alloys [e.g., René 142 by electron beam melting (EBM)] develop a γ’ precipitate structure without any postfabrication heat treatment (98). New alloys can be explored to achieve highly innovative precipitation sequences in the as-deposited conditions. One example is Al-Sc, which achieves refined precipitates by taking advantage of the substantial supersaturation state (i.e., increased k) of the matrix provided by the AM processing (99).

**Figure 8**
Example of banding in microstructure that is related to microstructural scale effects, as seen in Ti-6Al-4V. Adapted with permission from References 73, 94, and 131.
Similar results have been observed in Ti/TiB composites (100) and Er₂O₃-reinforced Ti (101), in which a highly refined distribution of thermodynamically stable dispersoids was achieved.

Various researchers have recognized the effect of texture and grain size on the precipitation of second-phase particles in the as-deposited microstructure. For example, Sun et al. (53) characterized M₂₃C₆ precipitates that form in an intragranular fashion and related both the precipitate formation and the overall properties to the columnar primary γ grains. Banerjee et al. (102) correlated the variant selection of grain boundary allotriomorphic phases with grain orientation in textured AM specimens. Ramirez et al. (103) demonstrated the possibility of producing precipitate or dislocation structures in low-purity Cu powder with a high concentration of Cu₂O precipitates.

In the preceding discussion in this subsection, compositional homogeneity of the molten pool prior to the onset of the phase transformation is assumed. Although such an assumption is generally valid when the convection mixing is sufficient to redistribute solute changes as described in Section 4, for elemental powder blends the situation depends upon both the input energy and the thermophysical properties of the material. For example, when refractory elements with relatively slow diffusivities are present as elemental powder, the microstructure of the as-built material is prone to containing partially melted particles that produce localized enriched zones around these particles (23, 24). Such zones may result in a compositionally induced variation of microstructure (e.g., crossing Tₐ), which leads to inhomogeneous distribution of phases (104). Such observations generally indicate that additional input energy (q) is required to sufficiently melt the material.

### 4. COMPOSITIONAL ASPECTS

To fully predict and control microstructure, it is necessary to understand both the composition of the starting material and the processing conditions (e.g., cooling rate, interfacial velocity). In AM, the material is a direct product of solidification, necessitating consideration of composition from multiple perspectives. These perspectives include (a) compositional variation due to the process (e.g., pickup from the atmosphere or loss of species through volatilization), (b) solute concentrations of phases that exceed equilibrium values due to solute trapping during solidification, and (c) the role that composition has on solidification (e.g., freezing range, partitioning, diffusivity in the liquid). These aspects are considered separately.

#### 4.1. Process-Induced Bulk Compositional Variation

Given the fact that AM is a solidification process, the final compositional certification moves downstream and is intimately coupled with the AM process. Although input feedstock can be certified, the AM process provides the opportunity to significantly modify the composition. Such modification can include both increases in interstitial elements that are present in the atmosphere (i.e., gettering) and losses due to differential vaporization of constituent elements.

Regarding the former, when processing is conducted under atmosphere, it is not unusual to observe concentrations of interstitial elements (e.g., oxygen, nitrogen, hydrogen) that are higher than in the composition of the feedstock. The problem can be exacerbated when one uses powder, which has a high surface area. These interstitial elements can have a significant impact on the resulting mechanical properties and microstructures. For example, in Ti-based alloys that exhibit a large solid solubility for oxygen, the oxygen pickup during the AM process [i.e., 0.032–0.205 wt% oxygen (74)] can lead to increases in yield strength and to loss of ductility (74). Such interstitial getting can push the composition of the deposited component beyond the typical design allowable. Although such pickup is largely viewed as undesirable, there may be some alloys or applications for which the atmosphere is used to intentionally increase the oxygen or nitrogen levels. For example,
some biomedical Ti-based alloys have increased oxygen levels (105); however, the oxygen in AM studies of these materials has not resulted in undesirable properties (106).

Regarding losses due to differential vaporization of constituent elements, elements with low vapor pressures preferentially evaporate. The temperatures of the molten pool are often high, and thus, to varying degrees, most elements evaporate. However, the end composition is governed by the variable weight loss of multiple elements, of which the low-melting-point elements suffer the most. The evaporation rate is a strong function of temperature and varies in a nonlinear fashion. Therefore, small temperature fluctuations caused by heat source power and frequency, spot size, and heat dissipation conditions can result in volatilization (107). For example, the reduction in Al content in the EBM of Ti-6Al-4V—which is conducted under vacuum, thus exacerbating the problem—can range between 10% and 15% (73, 108).

Most of the AM literature simply reports compositional differences in builds with respect to the starting material. This seemingly places the estimation or prediction of composition on a poor foundation. It would be useful to have a means of predicting both adsorption (gettering) of interstitial elements from the surrounding gas and the volatilization of elemental species from the molten metal. Given the relative dearth of papers discussing this topic in AM processes, one might consider reviewing welding or other solidification topics to understand this variation in composition. For example, a review of oxygen absorption in iron and steel provides equations to predict oxygen concentration as a function of temperature and oxygen partial pressure in a gas (109). Although this approach has a degree of usefulness, the characteristics of the AM process, which often do not reach equilibrium, must be considered. For example, Semiatin et al. (110) established kinetics models for evaporative losses under vacuum points and based their approach on the flux at the free surface of the melt \( J_s \) by assuming the Langmuir equation (111), expressed for the \( i \)th species as

\[
J_s = X_i P_i^a \gamma_i \sqrt{\frac{M_i}{2\pi RT}},
\]

where, for the \( i \)th species, \( X \) is the mole fraction, \( P_i \) is the vapor pressure at absolute temperature \( T \), \( \gamma \) is the activity coefficient in the liquid melt, \( M \) is the molar mass, and \( R \) is the gas constant (83.2 ergs/degree). Importantly, the paper by Semiatin et al. points to the consideration of atomic flux across the liquid/gas interface, which can be fundamentally treated by the Langmuir equation. The Langmuir equation, although derived for the purposes of evaporation and used by Semiatin et al. for evaporation, can describe condensation and adsorption equally well. The original form (111) is given as

\[
m = \sqrt{\frac{M_i}{2\pi RT}} \cdot p_i,
\]

where, in addition to the terms described above, \( m \) is the mass flux of a gas toward the surface in question and \( p_i \) is the partial pressure of species \( i \). As both Equations 2 and 3 and Figure 9 make clear, there is less pickup at higher temperatures. This is due to the more dominant inverse effect that temperature has on the density of the gas at the surface relative to the less dominant effect that temperature has on the velocity of the gas. However, neither Equation 2 nor Equation 3 captures time available for atomic flux, which (generally) increases with temperature. By reviewing the level of oxygen pickup for laser-based powder processes (e.g., an especially poor \( \sim 320 \) ppm (74) due to a water leak) of Ti-based alloys, and considering the probable temperature of the molten pool, melt pool size, and scan speeds (12, 17, 24, 73, 112, 113), one can calculate an \( n \) (\( n = m \cdot A \)) of \( \sim 2.61 \cdot 10^{-6} \) g/s. Furthermore, by considering an order-of-magnitude estimation of the cooling rate at the centerline of moving heat source problems (114), one can couple the mass flux to the thermal gradient and predict the oxygen pickup for a given melt pool size, material,
velocity, power, and so forth. The change in concentration can be represented as either $m$ or a calculated change in concentration for each time step. Panels a–c of Figure 9 show such an example, along with curves showing the effect of the input variable on gettering. Interestingly, using these variables for Ti, one calculates the total increase in oxygen to be $\sim 275$ ppm, very close to that observed elsewhere (74).

Thus, the Langmuir approach (111) is suitable for predicting both interstitial adsorption and evaporation. Although the latter was reported by Semiatin et al. (110) and was incorporated by others (73, 115), to the best of the authors’ knowledge, this presentation of the Langmuir equation is the first to predict interstitial adsorption in AM metallic structures. Importantly, the process describes a condition in which the surface-mediated flux, and not other kinetics, is the rate-controlling step. There appears to be sufficient convective mixing in the liquid phase (74) to affect a chemically homogeneous melt pool prior to solute redistribution during the solidification process. Care must be taken in predicting or measuring the melt pool temperature, as the temperature impacts $m$ directly, as shown in Equation 3, and indirectly by increasing the surface area of the molten pool, given the influence of temperature on liquid metal surface tension. Thus, to control composition (both evaporation and solute pickup), it is necessary to set the processing conditions such that the degree of superheat is minimized. With these tools, it should be possible to specify more accurately the composition of the starting material to achieve the desired postdeposited composition if the temperature of the molten pool and the atmosphere or vacuum can be controlled.

### 4.2. Process-Induced Nonequilibrium Partitioning and Subsequent Effects

The high velocities of the liquid/solid interface and the cooling rates with AM are often consistent with definitions of rapid solidification. These far-from-equilibrium structures allow for significant supersaturations of solid solutions derived from the $L \to S$ phase transformation. Such extended
solid solutions offer property benefits. For example, Tomus et al. (99) demonstrated increased solid solubility in the Al-2Sc binary system by using an electron beam–based AM approach. They showed a higher level of mechanical properties than could be achieved using a conventionally solution heat-treated and aged specimen.

Under such far-from-equilibrium conditions, solute trapping can occur. Solute trapping originates at the liquid/solid interface when the velocity of the moving boundary is faster than the diffusivity of the solute atom in the liquid phase (116). According to this solidification model developed by Aziz (116), the following condition must be satisfied for solute trapping to occur:

$$V \gg \frac{D_{\text{liquid}}}{a_0}.$$  

Here $V$ is the interface velocity, $a_0$ is the interatomic spacing during growth, and $D_{\text{liquid}}$ is the diffusion coefficient of solute in liquid. $V$ is equivalent to the $R$ described in Section 2.3. If this condition is satisfied, solute trapping occurs in the liquid phase and results in extended solid solubility.

The velocity of the interface, $V$ (or $R$, or $u$), is fastest along the maximum thermal gradient ($G = |\nabla T|$). By using the relationships given in Section 2.3, the model of Aziz (116) can be rewritten as

$$V = R = \frac{1}{|\nabla T|} \frac{\partial T}{\partial t} \gg \frac{D_{\text{liquid}}}{a_0}.$$  

Interestingly, the maximum thermal gradient (typically) occurs in the $z$-direction due to the fact that the highest heat extraction rate is associated with conduction as opposed to radiation or convection. This high heat extraction rate in the $z$-direction is directly related to the strong texture observed in AM materials (i.e., $<001>$ fiber texture $\parallel z$-direction). Thus, the solute trapping is expected to be greatest at the bottom of the molten pool. In fact, this solute trapping has been linked to the microstructure observed in cross section; this microstructure is banded (i.e., fish scale with regard to the variation of beam directions across layers) and inhomogeneous (18).

One manifestation of solute trapping and the resulting fish scaling is the precipitation of nonequilibrium phases for a given bulk composition. The work of Thijs et al. (18) showed this phenomenon in laser melting of Ti-6Al-4V powder (see Figure 10a), for which the concentration of Al in some regions reaches 25 at%, which triggers the precipitation of the Ti$_3$Al phase (see

![Figure 10](https://example.com/figure10.png)

**Figure 10**

Example of banding in microstructure that is related to solute partitioning and the subsequent evolution of different phases (here, an ordered $\alpha_2$ phase in Ti-6Al-4V). Adapted from Reference 18.
Figure 10b). Tang et al. (22) observed similar partitioning. The work of Tang et al. showed that both selective vaporization and solute trapping can lead to more pronounced compositional variation across the banded microstructure, which impacts the phase stability of the deposited material.

Although these bands are characteristic of AM deposits and provide evidence of solute trapping, supersaturated solid solutions can exist throughout the deposits. As such extended solid solution is inherently not in equilibrium, the supersaturation decomposes and leads to an ultrafine distribution of precipitates throughout the deposited material. Early work in this area involved Ti-B systems; Banerjee et al. (100, 117) showed that the decomposition of a supersaturated B concentration resulted in the precipitation of ultrafine Ti-B particles, including some that are 5–10 nm long (100).

5. A FRAMEWORK

Energy density, which incorporates the travel speed and metrics of melt pool geometry, can be conceptually related to Rosenthal’s approximation (or a modified approach by Ashby & Easterling for a diffuse heat source). Energy density, as described elsewhere in this article, captures thermophysical properties (e.g., melting point, heat capacity, and thermal conductivity) as well as thermodynamic parameters (e.g., the enthalpy of mixing for elemental powders). This single term is useful, as it parameterizes processing space and can be related to each of the microstructural features discussed above. This term is presented as the independent variable for the microstructural features described in this article and is presented as a conceptual framework in Figure 11a. Notably, for some microstructural features (e.g., unmelted particles), there is a minimum energy density required to avoid/eliminate the formation of that feature, whereas for other variables, there will be a maximum energy density beyond which features (e.g., hot tearing) may be expected. Some examples are provided in Figure 11b–d.

5.1. Macro-Level Microstructural Features

With respect to discontinuities, sufficient energy is required to melt all of the input material. Thus, there is a minimum energy density with respect to porosity, unmelted material, and lack of fusion (assuming proper path planning) (see Figure 11b). For some materials, there may exist a maximum energy density above which microcracks originating from hot tearing occur. Regarding residual stress, the degree of residual stress is related to the degree of input energy, which establishes the thermal field in the liquid and solid material. Texture, which is often observed in AM materials, is related to the thermal gradients in the liquid during solidification. Texture can be modified through establishing additional heat transport mechanisms or modifying composition.

5.2. Micro-Level Microstructural Features

Although the columnar grain structure dominates the microstructures reported in the AM literature, various authors have shown that equiaxed grains, cellular-to-equiaxed transitions, or zigzag structures are possible (18, 129). Zigzag structures appear when speed is increased (i.e., energy density decreases). The presence of equiaxed grains is strongly coupled with composition, most probably through differences in constitutional supercooling. The cellular-to-equiaxed transition is attributed to multiple heat transfer modes operating or to strong convective forces in the liquid state. Generally, $G (G = |\nabla T|)$ is proportional to the input power, and $R (R = \frac{1}{D} \frac{dT}{dt})$ is inversely proportional to input power and directly proportional to the velocity of the heat source relative to the substrate. These two parameters govern not only grain morphology (lower energy density is related to a larger $R$) but also solute partitioning, supersaturation, and precipitation (see
5.3. Compositional Aspects

In addition to solute partitioning, the loss and gettering of elements are also directly related to the energy density (see Figure 11d). In addition to the temperature term presented in the Langmuir equation, the time in which any given surface area can conduct the transfer of atoms is inversely proportional to the velocity of the heat source. Thus, for lower energy densities, there is less loss and less gettering.

6. TAKEAWAYS, OPPORTUNITIES, AND LIMITATIONS

On the basis of the interaction between processing, composition, and microstructure and the attending relationships between composition, microstructure, and properties, observing...
characteristics common to AM metallic materials is possible. Although the article describes the fundamental underpinnings of these characteristics, it is also possible to suggest strategies by which the microstructural features may be controlled and cases in which such control may not be possible. Such salient connections are made below.

6.1. Microstructural Discontinuities

There is a clear relationship between the process parameters and inhomogeneities. Such discontinuities originate within the melt pool or via associated thermal distortions. The opportunity is that the material-specific thermophysical properties and thermodynamic terms are important and can be tailored by changing alloys and the nature of the starting material (e.g., prealloyed versus elemental blends). The limitation is the minimum amount of energy required to process a fully dense material. If this minimum energy density exceeds a threshold for another microstructural feature (e.g., grain morphology), it will be impossible to produce the desired structure as a fully dense component without altering the process.

6.2. Residual Stress

Methods exist to predict and characterize the residual stress of AM materials. The residual stress generally varies from tensile to compressive states within the build. For some materials, the residual stress is sufficient to result in major distortions and microcracking.

6.3. Texture/Grains

A preferential texture is present in many AM metallic structures. This texture is the result of preferential growth along the largest temperature gradient. At certain temperature fields and solidification velocities, it is possible to enter regimes that promote equiaxed structures. Composition does impact the formation and type of texture. The interactions between \( G \), \( R \), and \( X \) can be used to understand and predict microstructures that evolve. The texture is tenacious and impacts the mechanical properties. Further research efforts into the influence of composition on the anisotropic liquid/solid interfacial energy and stiffness may lead to strategies to engineer texture (and hence strength) locally. New research into whether substrates can promote epitaxial growth when the thermal gradient term is less important. However, to understand \( G \) and \( R \), all local melt pool physics must be sufficiently captured.

6.4. Phases

The far-from-equilibrium nature of AM promotes metastable phases in many systems. The subsequent thermal cycling due to the deposition of additional layers can result in a spatially varying microstructure, in which the phases present, their size, and their composition may vary. In some systems, the far-from-equilibrium nature of the process allows highly refined precipitates to be affected. Such precipitates may be beneficial for certain properties and cannot easily be produced using conventional approaches. By considering the thermodynamic driving force for a given phase transformation, as well as the kinetics, it should be possible to engineer phase stability locally by modifying composition.
6.5. Compositional Variation

AM processes induce both bulk and local compositional variations. Bulk variation includes both preferential loss of volatile species and gettering of interstitial elements. Such variation necessitates a rethinking of compositional certification for end-use AM processes, for which the compositional certification falls, in part, to the supplier of the component. However, compositional variation can be predicted on the basis of the Langmuir equation by considering flux of atoms at the surface of the molten pool. The local compositional variation is related to the solidification process and can result in compositionally inhomogeneous materials. In addition, and importantly, the ability to control the feed rate of the incoming material means that composition can be independently controlled in a spatial manner. Such an engineered bulk compositional variation allows for local tailoring of composition, microstructure, and properties (102, 118–125).

Summary Points

1. The hierarchical nature of a microstructure can be understood by considering the evolution of the thermal fields with respect to time and position. The hierarchical microstructure includes discontinuities, residual stress, texture, and grain size or morphology.

2. Texture can be controlled by varying both processing and composition.

3. The bulk compositional variation from the starting material feedstock can be understood by considering mass transport at the liquid/environment (e.g., air, inert atmosphere, vacuum) interface.

4. The compositional variation in the melt pool, and consequently the resulting phases that form in the microstructure, may be understood by considering partitioning. Both the solute partitioning and the resulting phase variation can be attributed to macroscale discontinuities, including specifically the fish-scale effect.

5. Where current literature on AM is far from complete, fundamentals of solidification and welding provide valuable information.

6. Modeling approaches exist to accommodate many, but not all, aspects of AM. The degree of completeness is related to the details of the specific AM process.

Future Issues

1. As discussed above, the AM process is inherently a highly localized solidification process. The preponderance of peer-reviewed literature considers the microstructure in either the postprocessed state or the postprocessed and heat-treated state. This is due to the dearth of sophisticated characterization tools for characterizing the material in real time (i.e., during deposition).

2. Advanced techniques, including synchrotron diffraction, are required to understand the evolution of microstructure during AM. Research conducted using such tools is expected to provide tremendous insights into AM and to validate models.

3. Multisignal real-time process monitoring is required to capture indications of the macroscale discontinuities. It may be possible to also capture indications of texture development by using real-time process monitoring.
4. The ability to accurately predict thermal fields and thereby control composition or microstructure in a part should enable location-specific properties to be engineered into unitized structures.

5. As noted in Section 1, this article excludes any discussion of the influence of input material characteristics (e.g., particle size, size distribution, morphology) on the resulting microstructure. This lack of discussion is partially due to the numerous approaches used to characterize the powder and the absence of an accepted set of metrics for powder for AM.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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10. Provides details of melt pool physics, including the importance of the vapor, in additive manufacturing.

18. Discusses unusual microstructural features, including the zigzag pattern.


76. Shows deposition of a low-modulus metallic alloy for potential incorporation into biomedical implants.
90. Reports on the efforts to deposit bulk-metallic glasses using additive manufacturing.


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