Heat-Resistant Intermetallic Compounds and Ceramic Dispersion Alloys for Additive Manufacturing: A Review

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Many industries such as aerospace, power generation, and ground transportation demand structural materials with high specific strength at elevated temperatures. Up until now, many types of heat-resistant materials including Ni-based superalloys, intermetallic compounds, and dispersion-strengthened alloys have been developed for specific applications in these industries. Moreover, with the recent development of additive manufacturing techniques, these industries can now benefit from the rapid prototyping abilities, geometric freedom, and increased mechanical properties that can be achieved through various additive manufacturing processes. With this in mind, the progress made in additive manufacturing of heat-resistant intermetallic compounds and ceramic dispersion alloys is herein examined. A brief introduction is provided on the target industries, applications, and the compositions of heat-resistant alloys of current research interest. Then, recent research on heat-resistant intermetallic compounds and ceramic dispersion alloys fabricated by additive manufacturing processes such as laser powder bed fusion, laser direct energy deposition, and electron-beam powder bed fusion are reviewed with information provided on microstructure, processing parameters, strengthening mechanisms, and mechanical properties. Finally, an outlook is provided with future research suggestions.

1. Introduction

The retention of mechanical properties at elevated service temperatures is important for structural materials in cutting edge industries such as aerospace, power generation, defense, etc. Intermetallic compounds (ICs) and ceramic dispersion alloys (CDAs) are frequently used in these industries or are seen as next-generation materials not only due to their heat tolerance (i.e., their good elevated-temperature strength, oxidation resistance, etc.), but also due to their excellent mechanical and physical properties such as high wear resistance, low density, etc., that make them well suited for certain applications. Generally, ICs are more suited to high-temperature operation than CDAs due to the higher melting point and superior mechanical properties retention and microstructure stability. However, ICs have a high material cost, and many compositions are brittle at room temperature, limiting their practical and economic usability for applications such as advanced aircraft jet engines. Meanwhile, CDAs offer relatively modest elevated-temperature strength, but are suitable for use in a broad range of industries due to the relatively low cost, acceptable ductility, and the ability to tailor mechanical properties through control of ceramic reinforcement addition.

ICs are different from common metal alloys since ICs have a defined stoichiometry and ordered crystal structure, which is independent of the crystal structure formed by the individual elements in the composition.[1] Furthermore, atomic bonding consists of not only metallic bonds, but also ionic or covalent bonds, increasing not only brittleness but also high-temperature strength retention.[2-4] ICs may be present as precipitates within a traditional alloy.[5] Moreover, ICs may be reinforced with non-IC components, forming composites.[6] In this review, only IC compositions that lead to IC formation for the entire part are considered. General Electric now uses Ti–48Al–2Nb–2Cr (48–2–2 or GE-48) to fabricate low-pressure turbine blades for the GEnx commercial aircraft engines.[7] The high specific strength at elevated temperatures of this IC allows for mass reduction, which contributes to 20% fuel consumption reduction, 50% noise reduction, and 80% NOx emissions reduction compared with prior engines.

CDAs are a type of metal matrix composite (MMC) where reinforcement consists of discrete ceramic particles.[8,9] Due to their unique combinations of high specific strength, dimensional stability at high temperatures, and minimum thermal stress retention, they have been used in space vehicle structural applications including truss fittings and electronic packages, and interest is growing for use in other areas such heat sinks, mechanism housings, and bushings.[10] However, the usability of ICs is usually restricted by their fabrication difficulty. Their inherent brittleness at low temperatures, high ductile to brittle transition temperatures (DBTTs), and high hardness often limits or eliminates the possibility of using conventional forming and machining operations.[11,12] Furthermore, the hard reinforcement particles in CDAs substantially
In this work, recent efforts and advances in LPBF, LDED, and EPBF of ICs and CDAs are reviewed to highlight strengthening mechanisms and material characteristics specifically associated with the additive manufacturing processes. Important defect-formation mechanisms are also discussed. Special attention is directed toward metallurgical behavior, microstructures, feedstock preparation, mechanical properties, and defect and phase control. Finally, a prospective is provided with suggestions for future research.

2. Intermetallic Compounds for Additive Manufacturing

2.1. Definition and Strengthening Mechanisms of ICs

Fundamentally, ICs are single- or multiphase compounds, which are composed of at least two metal elements forming ordered structures with bonding ranging from metallic to covalent or ionic, and the resultant crystal structure and physical properties of ICs are independent of the parent material. However, ICs differ significantly in crystal structure from pure metals, thus requiring Strukturbericht designations to describe their analogous prototype crystal structures. The mechanical properties of ICs are strongly influenced by the type of bonding, which depends on the valency and electronegativity differences between elements.

Due to the additional ionic bonding and formation of ordered structures, aluminides such as $\beta$-NiAl, $\gamma$-Ni$_3$Al, $\gamma$-TiAl, $\alpha_2$-Ti$_3$Al, B2-FeAl, and D0$_{3}$-Fe$_3$Al demonstrate high melting point and excellent high-temperature microstructure stability and oxidation resistance. However, the different atomic species form ordered arrangements, leading to superlattice structures with low symmetry and high resistance to deformation by dislocation motion, which causes low-temperature embrittlement whereby the failure strain and fracture toughness are low below the DBTT. Therefore, manufacturing and post-processing of these materials present challenges for industry due to high cracking and fracture potential.

2.2. Processing, Solidification, Defects, and Microstructure of Additive Manufactured ICs

In general, the cooling rate is much higher for LPBF, LDED, and EPBF compared to casting, and the layer-by-layer processing inherent to additive manufacturing also leads to a complex thermal history. However, cooling rate and thermal history also differ between the additive processes due to differences in the build-platform temperature, build-chamber environment, energy input, and material deposition method. For PBF processes, applied laser or electron-beam power and spot diameter, scan speed, hatch spacing, build-platform heating, and layer height control cooling rate, residual stresses, and densification. For LDED, these factors are controlled by laser power and scan speed, hatch spacing, layer increment, deposition speed, and feed rate. Fundamental differences between processes result in significantly different melt pool and microstructure characteristics for ICs and other materials.
The laser spot diameter generally ranges from 50 to 250 μm for LPBF and 0.3–3 mm for LDED and is often a physically set value.\textsuperscript{[33,32]} For EPBF, the focus offset is adjusted by changing the electromagnetic lens system current flow, and the resultant electron-beam spot diameter is often several hundred μm.\textsuperscript{[28,32]} A larger spot diameter results in energy distribution over a larger area, which means a higher laser or electron-beam power and/or lower scan speed are necessary for single-track powder consolidation in PBF processes.\textsuperscript{[13]} The larger laser spot diameter results in a larger melt pool for LDED compared to LPBF,\textsuperscript{[34]} and selecting a relatively larger spot diameter is more suitable for stable consolidation of thick powder layers in PBF.\textsuperscript{[13]}

Cooling rate is linked to the thermal gradient and thermal stresses during fabrication, where increased cooling rate alludes to higher cracking potential due to increased thermal stress during solidification. Furthermore, cooling rate is dependent on processing parameters in LPBF, EPBF, and LDED.\textsuperscript{[25,35–38]} In general, cooling rate increases with laser or electron-beam power and scan speed, assuming other parameters are kept constant. As previously stated, there are fundamental differences between additive processes, which affect the heat distribution within the melt pool and require different scan speed and laser power combinations to achieve high densification. For this reason, cooling rate and thermal stresses for optimized parameters vary between additive processes, and some processes are more suitable for crack suppression than others. Furthermore, the cooling rate differences between processes lead to different microstructures and nonequilibrium phase compositions. Depending on the thermal gradient and mass transfer kinetics, constitutional supercooling can result in planar, cellular, columnar dendritic, or equiaxed dendritic grain growth.\textsuperscript{[199]} Furthermore, the layer-by-layer processing causes thermal cycling of the previously fabricated layers, and the directional solidification promotes grain growth in the direction of the heat source, encouraging elongated grain structures and anisotropic mechanical properties.\textsuperscript{[40–44]}

Accordingly, the following subsections will examine how chemical composition and processing conditions affect the microstructure and crack formation in ICs, and how those factors can be controlled to create dense, crack-free IC components with desired microstructures.

### 2.2.1. Additively Manufacturing Binary ICs

In the case of LPBF and LDED of NiAl and FeAl binary alloys,\textsuperscript{[45–48]} cracking was noted to be an issue. When LPBF and LDED were applied to Ni 27.7 at% Al powder,\textsuperscript{[45]} both multilayer and single tracks fabricated with parameters optimized for high density contained a fine dendritic microstructure with little porosity. However, many irregular cracks were reported in multilayer samples, making the material unsuitable for structural use. X-ray diffraction (XRD) and scanning electron microscope (SEM) energy dispersive X-ray spectroscopy revealed identical phase composition for both LPBF- and LDED-fabricated samples, which consisted of mainly γ-NiAl. However, differences in minor phases existed between LPBF and LDED. In the case of LPBF fabrication, a relatively low amount of β-NiAl was present, which increased in content with lower scan speed. Meanwhile, the metastable phase Ni3Al was detected in LDED-fabricated samples. While the authors did not directly address the reason for the slight difference in phase composition, it was noted that LPBF led to stronger thermal cycling and higher thermal gradient compared to LDED, which produced a finer microstructure and influenced elemental segregation and phase generation.

LPBF fabrication of graded FeAl samples with Al content increasing from 10 to 40 at% was used to determine the maximum Al content for crack-free LPBF fabrication and to understand the associated phase formation.\textsuperscript{[46]} With Al content ranging from 6 to 24 at%, only the A2 phase (FeAl solid solution) was XRD identified and no cracking was noted. However, when Al was in the range of 32–39 at%, XRD indicated the formation of the B2-FeAl intermetallic phase. Al content in excess of 35 at% led to the formation of intergranular cracking, which appeared to coincide with B2 phase formation. The formation of Fe3Al (D03) was not reported for any of the tested compositions. As seen in Figure 2a,b, FeAl experienced a columnar to equiaxed transition during LPBF as the amount of Al in binary alloy increased. As described earlier in this section, constitutional supercooling was determined to be partly responsible for the different grain structures. It has been previously argued that an increase in the growth restriction factor $Q$ suppresses epitaxial grain growth from high thermal gradients.\textsuperscript{[49]} Therefore, the authors used $Q$ estimated using

$$Q = m(1 - K_0)$$  \hspace{1cm} (1)

to describe the degree of segregation and restriction effect of solute on new grain solid–liquid interface growth. In Equation (1), $m$ is the liquidus slope in the phase diagram, $c_0$ the alloy solute content, and $K_0$ the partition coefficient. As Al content increased from 0 to 40 at%, $Q$ increased from 0 to 28.7 °C, and this was shown to convert grains from a columnar structure to mixed and eventually equiaxed grains. A summary of results can be seen in Figure 2e. However, it should be noted that formation of equiaxed grains was not effective in inhibiting crack formation of this alloy, and crack-free samples could not be fabricated when Al content was increased over 35 at% seemingly due to formation of B2 phase.

In a similar study, LDED was used to fabricate FeAl samples with Al content increasing from 6 to 50 at%.\textsuperscript{[48]} With Al content of 6 at%, samples experienced severe warping and were considered to be unsuccessfully deposited; however, samples with 28 and 36 at% Al were fabricated crack free with low porosity. Meanwhile, samples fabricated with 50 at% Al contained severe cracking, which was attributed to brittleness of the B2 phase and high thermal stress during fabrication. In contrast to LPBF-fabricated samples, Fe3Al (D03) was not only present in the LDED-fabricated 28 and 36 at% Al samples, but it was the only phase detected in the 28 at% Al samples. In addition to Fe3Al (D03), the 36 at% Al sample also contained B2-FeAl, while the 50 at% sample contained only B2-FeAl. The differences between LPBF and LDED are explained by cooling rate. As previously demonstrated for Ni-27.7 at% Al,\textsuperscript{[45]} the higher LPBF cooling rate and thermal gradient compared to LDED promoted the formation of nonequilibrium phases. Furthermore, in a separate study where LDED cooling rate was varied,\textsuperscript{[50]} relatively high cooling rate formed A2-FeAl solid solution in FeAl with up to 34 at% Al. Meanwhile, relatively low cooling rate formed Fe3Al (D03).
when Al content was 25–34 at%. Clearly, the additive manufacturing method and the associated processing parameters have significant effect on phase formation, microstructure, and crack development.

Considering crack formation, this occurs in additively fabricated ICs for a variety of reasons. B2 structured compounds such as β-NiAl, B2-TiAl, and B2-FeAl as well as DO19-structured α2-Ti3Al have a limited number of slip mechanisms at low temperature\(^{[51–53]}\) and, therefore, have low ductility and poor fracture toughness. Even though γ-Ni3Al (D0\(_3\)) and Fe\(_3\)Al (D0\(_3\)) phases are ductile as single crystals, brittleness is seen in undoped polycrystalline material due to grain boundary and/or bulk material hydrogen embrittlement\(^{[54,55]}\). When the cooling rates are high and the thermal gradients are steep during various additive manufacturing process, high stress is caused due to localized material contraction and cold cracking occurs, as shown in Figure 3.\(^{[47,51,56,57]}\) In addition, solidification cracking is known to occur.\(^{[58–62]}\) The cause of solidification cracking for ICs is the presence of a thin liquid film during the final stages of solidification, which is easily ruptured by residual tensile stresses.\(^{[63]}\) However, steps can be taken to eliminate cracking during fabrication, such as IC alloying, build-platform preheating, and printing parameter control. Furthermore, post-processing of fabricated parts may also be used to repair cracks.

**Figure 2.** FeAl samples fabricated via LPBF. a,b,e) Change in grain size of FeAl alloy with increasing Al content and growth restriction factor \(Q\); c) Fe-rich side of FeAl phase diagram; d) XRD scan results. Regions 1, 2, 3, 4, 5, and 6 represent Al content of 6.2, 15.1, 23.9, 32.1, 35.4, and 39.1 at%, respectively. Reproduced with permission.\(^{[46]}\) Copyright 2021, Elsevier.
2.2.2. IC Alloying and Additive Manufacturing

While it is possible to control the microstructure by adjusting processing parameters for some materials,[43,44,63] fabrication of defect-free ICs is often reported for a relatively narrow material-dependent energy density range. However, the addition of alloying elements can greatly increase the range of acceptable processing conditions while affecting the IC's solidification and microstructure. This leads to significant differences in cracking propensity and mechanical properties. For example, in the NiAl system, Cr and Mo improve cracking resistance by forming an intergranular eutectic, while Cr and Co strengthen the β-NiAl matrix by precipitate formation and solid solution strengthening, respectively.[64–71] For the TiAl system, Mn promotes deformation twinning, increasing room-temperature ductility,[72,73] while Nb promotes α2 phase formation to give a lamellar microstructure and eliminate any unwanted B2 phase.[74,75] In the case of FeAl, the addition of Ti and B has been demonstrated to decrease cracking tendency by decreasing the DBTT and promoting grain refinement.[76,77] Hot isostatic pressing (HIP) has also been shown to successfully repair cracks. During HIP, high-pressure inert gas surrounding samples applies stress around defects, promoting shrinkage, while a temperature near the sample melting point promotes material sintering and crack healing. HIP also reduces porosity and fuses partially melted particles with surrounding materials.[64,70,71]

Gao et al.[43] studied LPBF of Ti–40Al–9V–0.5Y by keeping constant laser power of 200 W and varying scan speed from 100 to 1000 in 100 mm s\(^{-1}\) steps. At low scan speed, crack formation was prevented, yet a large amount of gas-induced porosity was present in samples due to keyhole collapse. As scan speed increased, melt pool changed to conduction mode which eventually eliminated gas porosity; however, crack density increased. The change in crack density with scan speed was demonstrated to be caused by a complex relationship between phase transformation and microstructure, which were affected by the change in melt pool cooling rate. In this particular example, cracks were present at 300 mm s\(^{-1}\) scan speed but were eliminated by decreasing to 200 mm s\(^{-1}\), which corresponds to 8.78 \times 10^6 K s\(^{-1}\) and 8.46 \times 10^4 K s\(^{-1}\) calculated maximum cooling rate, respectively. At the higher cooling rate, the grain structure was columnar and XRD-indicated solidification of

![Figure 3. Ni50Al50 (at%) fabricated by LDED using ](image)
>99% B2-TiAl due to a restricted diffusion-controlled phase-transformation mechanism. At the lower cooling rate, atomic diffusion was more favorable, allowing Y atoms to form YAl2 along the solidification front, which acted as heterogeneous nucleation sites for grain growth. This caused the grain structure to become mixed columnar and equiaxed. Phase formation was also significantly affected, reducing B2-TiAl content to 22.2–34.5 vol% and forming α2 phase (62.9–70.3%), γ phase (3.34–7.53%), and YAl2 phase (2.58–3.52%). As shown schematically in Figure 4, the combination of B2-TiAl phase reduction and formation of equiaxed grains contributed to improve ductility of the material and reduce cracking potential. This example highlights the advantage of alloying IC systems to develop a material suitable for LPBF.

In the case of Fe–30Al–5Ti–0.7B could be fabricated defect free with comparatively lower build-platform preheating temperature of 600 °C for LPBF and 400 °C for LDED. The additional B combined with Ti to form TiB2, which precipitated at L21 grain boundaries and within grains; however, in EPBF-fabricated Fe–28Al–5Ti–1.3B, TiB2 was only dispersed at matrix grain boundaries.

2.2.3. Impact of Processing Methods on Microstructure

LPBF, LDED, and EPBF all operate by melting metal powder to form solid layers, which are formed consecutively to build the final part. However, differences in cooling rate between these processing methods as well as build-platform heating have been reported to affect microstructure, defect formation, and mechanical properties.

LPBF[79,80] and LDED[81–83] were performed on a Ti–22Al–25Nb alloy, which has a composition that allows for precipitation strengthening via the orthorhombic O–Ti3AlNb phase. O-phase has excellent creep resistance, good elevated-temperature stability, effectively strengthens the B2 matrix, and compared with conventional α + B2 TiAl alloys, O + B2 alloys offer higher elevated-temperature mechanical properties.[84–86] However, the O-phase is less ductile and harder than the B2 matrix, resulting in stress concentrations and increased propensity for cracking, especially when O-phase is present with coarse morphology.[87] In the case of LPBF, the as-printed samples consisted mainly of Nb-supersaturated B2/β grains and 0.2 vol% fine O-phase. This is in stark contrast to LDED-fabricated material, which contained a B2 matrix, equiaxed α2 particles, and plate-like and lath-like O-phase. This is likely due to lower LDED cooling rate resulting in comparatively lower matrix supersaturation and larger precipitate formation. In LPBF-fabricated samples,[79,80] a small amount of fine O-phase was present at melt pool boundaries, a part of the melt pool that is known to undergo relatively slow solidification due to persistent heat input from melt pool center.[40] After the LPBF-fabricated sample was solution treated at 950 °C and aged at 700 °C for 6 h, acicular O-phase and α2 particles were present in the B2/β grains, with α2 also present at B2 grain boundaries.[79] For the LDED-fabricated material, solution treatment at 960 and 750 °C aging for 3 h caused precipitation of a greater amount of fine O-phase.[81] As seen in Table 1, Nb supersaturation of the B2 phase and low O-phase content had a significant impact for the LPBF-fabricated material, allowing for room-temperature ultimate tensile strength (UTS) of 973 MPa and elongation of 24.9%. However, the 650 °C tensile properties of the as-printed sample were relatively low, with UTS of 365 MPa and elongation of 0.4%.[79] Precipitation of O-phase through solution treatment and aging increased the 650 °C UTS to 749 MPa but significantly reduced the room-temperature properties of the as-printed sample were relatively low, with UTS of 365 MPa and elongation of 0.4%.[79] Precipitation of O-phase through solution treatment and aging increased the 650 °C UTS to 749 MPa but significantly reduced the room-temperature properties of the as-printed sample were relatively low, with UTS of 365 MPa and elongation of 0.4%.[79] Precipitation of O-phase through solution treatment and aging increased the 650 °C UTS to 749 MPa but significantly reduced the room-temperature

Figure 4. Grain structure and solidification behavior of Ti–40Al–9V–0.5Y fabricated via LPBF with laser scan speed of a) 300 mm s−1 and b) 200 mm s−1. Reproduced with permission.[40] Copyright 2020, Elsevier.
ductility. Meanwhile, LDED-fabricated material had relatively reduced Nb supersaturation of the B2 phase as alluded to by relatively greater volume of O precipitates. Comparable mechanical testing was not performed on LDED-fabricated samples; however, information presented by the authors showed reduced ductility in the as-printed state compared to LPBF-fabricated material in the same condition.[81]

One often suggested, yet infrequently applied, method of crack reduction for LPBF and LDED is higher-temperature build-platform heating.[71,88–90] For some ordered intermetallics, both yield strength and ductility increase up to a certain temperature,[55,91,92] which has been shown to decrease cracking tendency.[88,89] This is also where EPBF provides an advantage, as a much higher build-platform temperature is used than is currently typical for LPBF or LDED. This is necessary for EPBF as sintering powder particles together increase the electrical conductivity and assist in holding the part during fabrication.[35,93] Furthermore, it is thought that the high powder bed temperature

| Fabrication method and material [at%] | UTS [MPa] | Elongation, ε [%] | Compressive yield strength [MPa] | Heat-treatment condition | Test temperature [°C] |
|--------------------------------------|-----------|-------------------|---------------------------------|--------------------------|----------------------|
| LPBF Ni₄₁Al₄₁Cr₁₂Co₆[64]             | Not tested| Not tested        | 685                             | Aging                    | 600                  |
| LPBF Ni₄₁Al₄₁Cr₁₂Mo₆[71]             | Not tested| Not tested        | 750[6]                          | HIP                      | 700                  |
| LPBF TiAl₁₂₂Nb₂₅[79]                 | 973       | 24.9              | Not tested                      | As-printed               | RT                   |
| LPBF Ti₄₈Al₅₁Cr₇Mo₄[79]              | 554       | 5.75              | Not tested                      | As-printed               | 750                  |
| LPBF Fe₃₀Al₁₀Ti[76]                  | Not tested| Not tested        | 545[6]                          | As-printed               | RT                   |
| LPBF Fe₃₀Al₁₀Tiₐ₇[76]                | Not tested| Not tested        | 940[6]                          | As-printed               | RT                   |
| EPBF Ni₁₇Al₂₂Cr₂₆Mo₃₀.₃Re₁₇Ta (IC21)[63] | 920[6] | 6[6]              | Not tested                      | As-printed               | RT                   |
| EPBF Ti₄₈Al₂₂Cr₂₂Nb[107]             | 710       | Not tested         | Not tested                      | As-printed               | RT                   |
| EPBF Ti₄₈Al₂₂Cr₂₂Nb[107]             | 470[6]    | 1.1[6]            | Not tested                      | Solution                 | RT                   |
| EPBF Fe₂₈Al₅₁Ti₁.₃B[77]              | 790[6]    | 1[6]              | 800                             | As-printed               | RT                   |
| EPBF Fe₂₈Al₅₁Ti₁.₃B[77]              | 470[6]    | 1.1[6]            | 690                             | HIP                      | RT                   |
| EPBF Fe₂₈Al₅₁Ti₁.₃B[77]              | 400[6]    | 35[6]             | 400                             | HIP                      | RT                   |

Table 1. Mechanical properties and corresponding processing parameters for additively manufactured intermetallic compounds.

a)LPBF: laser powder bed fusion; EPBF: electron-beam powder bed fusion; HIP: hot isostatic pressing; RT: room temperature. b)Denotes values taken from a graph.
is the chief factor in EPBF demonstrating outstanding capability for producing crack-free TiAl alloys and other IC components, including those with high brittle phase content. However, the high build-platform temperature also results in in situ heat treatment, changing the mechanical properties.

EPBF fabrication of TiAl alloys has generally focused on Ti–xAl–2Cr–2Nb,[94–99] which is an alloy currently used for commercial aircraft turbine blades.[7] Since EPBF operates above the DBTT for TiAl, which is in the range of 700–800 °C,[100] EPBF offers a lower residual stress and cracking potential compared to LPBF or LDED. However, the service temperature of conventionally fabricated TiAl alloys is considered to be 700–900 °C,[101] and high EPBF operating temperatures affect the microstructure and mechanical properties.[102] The microstructure determines the tradeoff between high-temperature and room-temperature mechanical properties in TiAl alloys,[103] and high build-platform temperatures have been shown to cause in situ annealing, microstructure evolution, and phase transformation in the previously deposited layers over time.[96,97] Chen et al.[96] investigated microstructure and hardness of EPBF-fabricated Ti–47Al–2Cr–2Nb alloy and noted variations in the in situ heat-treatment microstructure at different locations on the build due to the 1060 °C build-platform temperature as described in Figure 5. The in situ heat treatment of parts is considered to occur in two stages. The first stage lasts only a few layers and is caused by the electron-beam consolidating powder to form new layers. Heating and cooling in this stage occur relatively quickly. The second in situ heat-treatment stage occurs due to the continuous high build-platform temperature, and the heat-treatment duration of this stage depends on the height from the base substrate. Figure 5b–e shows the microstructure change that occurs due to the heat treatment at different heights of a 20 mm high EPBF-fabricated part. The 20 mm height represents the last deposited layers, which experiences stage 1 heat treatment and furnace-type cooling, resulting in a near-lamellar microstructure consisting of mostly γ phase. At the 19 mm height, the part was held at the build-platform heating temperature for 0.2 h, which caused obvious change to duplex

Figure 5. Ti–47Al–2Cr–2Nb fabricated via EPBF. a) Thermal history at different build heights; corresponding electron backscatter diffraction (EBSD) image showing transverse-section microstructures and phase maps at b) 20, c) 19, d) 15, e) 5 mm distance from the build platform. Reproduced with permission.[96] Copyright 2018, Elsevier.
microstructure and formation of additional precipitates. The trend continued to the bottom of the part, and room-temperature hardness testing revealed hardness from 1 to 19 mm height was approximately 341.8–359.6 HV; however, it increased to 393.7 HV at 20 mm height. In EPBF-fabricated Ti–48Al–2Cr–2Nb, similar hardness testing response was noted, and tensile testing revealed higher UTS of tensile bars made from the top of fabricated cubes.

2.3. Mechanical Properties of Additively Manufactured ICs

Table 1 lists measured mechanical properties of additively manufactured IC alloys. These alloys were fabricated with compositions and processing parameters leading to low defect formation.

As seen in Table 1, a wide range of mechanical properties are possible, depending on the material and manufacturing process. For example, LPBF-fabricated TiAl22Nb25 provides exceptionally high room-temperature tensile strength and elongation in the as-printed condition. From the viewpoint of high-temperature mechanical properties, NiAl and TiAl alloys provide increased strength compared to Fe3Al, which experiences a substantial strength decline when exposed to temperatures exceeding 600 °C. However, iron aluminate alloys are still important materials since they present significant cost advantages while having low density and demonstrating good oxidation and sulfur resistance.104 When comparing LPBF-fabricated nickel aluminiides and titanium aluminiides with nickel-base superalloys such as IN718,105,106 the yield and ultimate stresses are often similar. Furthermore, the density of IN718 is 8.192 g cm⁻³, which is higher than that of Ni₄₋₂Al₅₋₂Cr₇Mo₂⁺₇ (≈5.78 g cm⁻³), Ti–48Al–2Cr–2Nb107 (3.9 g cm⁻³), or other NiAl- and TiAl-based alloys.108 This presents a significant potential for reduction of component mass while retaining required mechanical strength.

ICs tend to have low ductility, especially at room temperature, and this has been a severe limitation preventing widespread use of these materials. An advantage of additive manufacturing is that it removes the need for using deformation processing steps to reach a net-shape component, thus reducing the ductility requirement for the material. This makes EPBF an especially attractive process for a wide range of relatively brittle to ductile ICs; however, from the viewpoint of LPBF and LDED, an excessively brittle material is difficult to fabricate without severe cracking. Therefore, increasing ductility through alloying or process control would have the dual effect of enabling easier LPBF and LDED fabrication and increasing the damage tolerance of the final component in the form of higher fracture resistance.

3. Ceramic Dispersion Alloys

3.1. Reinforcements and Matrices of CDAs for Additive Manufacturing

CDAs are a type of MMC, which is a composite material composed of a metal matrix and nonmetal reinforcement.109 While MMCs may use non-ceramic reinforcement and may be continuously (monofilament fibers) or discontinuously (short fibers, whiskers, particles) reinforced, the metal matrix of CDAs is discontinuously reinforced with ceramic particles.8,9 For traditionally fabricated CDAs, the addition of ceramic particles leads to a relatively modest strength increase. Nevertheless, mechanical properties can be easily tailored to suit different engineering applications by choosing the appropriate matrix, reinforcement, and manufacturing process. Considerations for additively manufactured CDA reinforcement selection and processing routes are different than those for casting processes due to the unique interaction of laser- or electron-beam heat source, particle stirring due to Marangoni flow, and high solidification rate.

To produce the powder feedstock, two approaches are frequently used. The most common approach is introducing the ceramic particles ex situ into the matrix by mechanically mixing a commercially available matrix alloy powder with ceramic particles. This method of ceramic particle introduction makes it easy to tailor the reinforcement volume; however, thorough mixing is required to achieve a homogeneous reinforcement distribution. Alternatively, an alloy with appropriate composition for in situ ceramic reinforcement formation can be cast and subsequently gas atomized. Ideally, the melt would be thoroughly stirred during the process, which would favor a homogeneous ceramic particle distribution within the resulting powder. However, issues may arise due to the gas atomization nozzle becoming clogged with the ceramic reinforcement.110 In addition, secondary reactions may occur during the melting and gas atomization steps, making the resulting powder composition unclear. Examples of ex situ reinforcements and matrices increasing elevated-temperature mechanical properties of additively manufactured CDAs include micro-size TiCN in an Al matrix,111 TiB₂ in a steel matrix,112 TiC in a steel matrix,113 and nano-size TiC in steel and Ti matrices.114 Pre- alloyed powder containing Ti and B has also been successfully used to form TiB₂ reinforcement in an Al matrix110,111. These studies focused on LPBF fabrication; however, the trends are likely to be transferable to LDED116–119 and EPBF120–122 fabrication due to the mechanisms behind the elevated-temperature mechanical properties increase, as described in detail later in Section 3.3. Although their high-temperature mechanical properties have not yet been evaluated, other CDAs have also been successfully additively manufactured. Examples include SiC,123 Al₂O₃,124 Fe₃O₅,125 and TiN126,127 in Al matrices; V₆C₇,128 CeO₂,129 and WC130,131 in steel matrices; TiN132 and Mo₂C133 in Ti matrices.

Of the available ceramic reinforcements, TiCN, TiC, and TiB₂ are noted for causing little or no detrimental in situ reactions in Ti-, steel-, and Al matrices. However, other ceramic particles can form brittle compounds by reacting with the matrix during additive fabrication. For example, during fabrication of SiC-reinforced Al matrices, SiC can degrade in the melt and cause unstable and brittle Al₄C₃ formation, leading to decreased mechanical properties of the CDA.123,134 Similarly, SiC added to Ti matrices can form the undesirable compound Ti₃Si₄C₃ while V₆C₇ added to steel matrix can be broken down to form VC and (Fe, Cr, Mo, Ni)₃C phases.128 Even though reactions can occur between reinforcement and matrix, it is possible to have some degree of control over this phenomenon. For example, the melt pool and immediate area is exposed to high temperatures for a very short time during additive manufacturing, which reduces undesirable reactions between the matrix and reinforcement. This elevated-temperature exposure can be
controlled by adjusting the applied energy density. Furthermore, EPBF may reduce the tendency for ceramic reinforcement melting and matrix reaction. Astfalck et al. investigated the influence of laser energy density on LPBF-fabricated Al–12Si powder containing 10 vol% SiC and found that increasing the applied energy density from 20 to 80 J mm\(^{-3}\) reduced the SiC content in the as-printed CDA from \(\approx 9\) to \(<4\) vol%, as seen in Figure 6. The authors hypothesized that SiC particle degradation occurred when the phase temperature exceeded 2800 °C. As described in Section 3.2 and shown in Table 2, SiC has higher laser absorptivity than the Al matrix, even though this is material dependent and cannot be taken as the general case. Nevertheless, it is possible that the higher laser absorptivity of SiC compared to matrix promoted localized particle overheating. SiC has significantly lower electrical conductivity compared to Al matrix, and lower electrical conductivity would reduce the amount of local heating by the EPBF electron beam. At this time, little research can be found on this topic. Huang et al. compared laser-beam welding (LBW) and electron-beam welding (EBW) of Al6061 with 1–20 wt% SiC and concluded that the addition of SiC did not affect electron-beam energy absorption, but significantly increased laser-beam absorption. However, unmelted SiC tended to increase melt viscosity, and significant defects were present in the welds, particularly for EBW.

### 3.2. Solidification, Defects, and Microstructure of Additively Manufactured CDAs

Introducing ceramic particles into a metal matrix can significantly affect the melt pool due to changes in specific heat capacity and laser absorptivity. Furthermore, ceramic particles have a melting temperature higher than that of the matrix and tend to remain in solid form as the matrix melts and solidifies around them, increasing melt viscosity and activating several important metallurgical mechanisms that directly influence solidification, defect formation, and mechanical properties of additively fabricated parts.

The effect of ceramic particles depends on the volume present in the melt as well as the matrix and ceramic considered. As seen in Figure 7, increasing additions of TiB\(_2\) from 5 vol% to 10 vol% in 316L cause the LPBF melt pool to become wider yet shallower when processed with the same parameters. Meanwhile, adding 10 wt% TiB\(_2\) or SiC to AlSi10Mg causes an increase in both width and depth of the melt pool. This can be explained by the effect ceramic particles have on LPBF and LDED laser absorptivity as well as the melt pool Marangoni flow during LPBF, LDED, and EPBF.

Non-oxide ceramic reinforcements tend to have a much higher laser absorptivity compared to the metal matrix, as shown in Table 2. When non-oxide ceramic particles are added to a metal powder, the laser absorptivity increases, which increases the temperature and accumulated energy in the melt pool during laser processing, increasing both width and depth of the melt pool. However, during fabrication, the large thermal gradient activates Marangoni flow, the intensity of which can be described as

\[
Ma = \frac{\Delta \sigma L}{\mu \nu k}
\]

In Equation (2), \(\Delta \sigma\) is the surface tension difference (N m\(^{-1}\)), \(L\) is the melt pool length, \(\nu k\) is the kinematic viscosity, and \(\mu\) is the dynamic viscosity.
\[ \mu = \frac{16}{15} \sqrt{\frac{m}{kT\gamma}} \]  \hspace{1cm} (3)

where \( m \) is the atomic mass, \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( \gamma \) is the surface tension. According to Equation (3), a higher laser power can reduce melt viscosity by increasing the temperature of the melt, partially offsetting any increase in melt viscosity due to ceramic particles addition. In Equation (2), the kinematic viscosity \( \nu_k \) can further be considered as dynamic viscosity divided by melt density. Due to the Gaussian distribution of laser or electron-beam heat source, the temperature is highest near the center of the irradiated area and lowest at the solid–liquid interface at the edges of the melt pool. Because surface tension increases as the melt temperature decreases, the surface tension will be highest at the melt pool edges.[142] This causes liquid to flow radially from the irradiated area toward the edges, a phenomenon that has been demonstrated to cause a shallower and wider melt pool.[146] On the one hand, an increase in temperature gradient, due to increased laser energy absorptivity, will increase \( \Delta \sigma \) and Marangoni flow intensity. On the other hand, one can see that an increase in melt dynamic viscosity, due to the presence of solid particles, would decrease the Marangoni flow intensity and contribute to a melt pool that may not be wide enough to produce sufficient overlap without scanning parameter adjustment.[147]

To achieve optimal and uniform mechanical properties across the fabricated part, homogeneous distribution of reinforcement is necessary, and this is not guaranteed by additive manufacturing due to the particle accumulation structure (PAS) mechanism.[112,148] During fabrication, the oscillatory thermocapillary effect causes the ceramic particles to circulate within a ring vortex in the melt pool. As shown in Figure 8, previous homogeneously distributed ceramic particles will tend to form agglomerates during solidification. The PAS mechanism can be inhibited by increasing the intensity of the Marangoni flow through higher energy input during printing, thus achieving a more homogeneous ceramic particle distribution.

Ceramic particles remaining in the melt as solids act as heterogeneous nucleation sites for grains, forming a refined equiaxed grain structure, which reduces anisotropy and allows LPBF- and LDED-fabrication of notoriously crack-prone alloys such as Al2024, Al6061, and Al7075.[116,117,137,149,150] The grain refinement effect is illustrated in Figure 9. The high cooling rate during laser fabrication favors the formation of a coarse columnar grain structure in Al, Fe, and Ti matrices, which is known to induce solidification cracking in non-weldable alloys.

Figure 7. Scanning electron microscope (SEM) images showing etched microstructures of LPBF-fabricated samples composed of 316L-TiB₂ with a) 5 vol% and b) 10 vol% ceramic addition[112]; c) AlSi10Mg with no ceramic particles, d) 10 wt% SiC, e) 10 wt% TiB₂, and f) variation of melt pool dimension. Reproduced with permission.[140] Copyright 2019, Elsevier.
Solidification cracking is caused by the primary solidifying grains enriching the remaining liquid and forming a eutectic. The semi-solid eutectic has low strength, and if insufficient liquid is present or if feeding is blocked, the liquid film can rupture as the primary grains shrink or move at the terminal stages of solidification. This type of cracking is affected by alloy composition and grain size. Removing eutectic-forming elements from the alloy eliminates the eutectic and disables the cracking mechanism. In contrast, increasing the quantity of eutectic-forming elements provides a greater amount of intergranular eutectic and eliminates cracking. A refined equiaxed grain structure decreases the crack sensitivity relative to a coarse columnar structure by forming a large grain boundary area relative to the grain size, decreasing relative solidification shrinkage and the chance of liquid channel blockage.

Grain refinement depends on the size and elemental composition of the ceramic particles being added as well as the matrix. In general, the grain-refining potential is inverse to reinforcement particle size.[151] Therefore, for a given volume of added ceramic particulate, smaller particles would be more effective at grain refinement. AlMangour et al.[113] separately added 15 vol% 2–12 and 50 nm TiC particles to 316L powder, which reduced the average grain size from 28.18 to 8.27 and 6.99 μm in LPBF-fabricated samples, respectively, and both particle sizes were successful in converting the grain structure from columnar to equiaxed. However, additional mechanisms may contribute to grain refinement. Depending on the processing parameters, matrix, and reinforcement, sufficiently high temperatures during LPBF can cause partial melting of ceramic particles and a reaction with the matrix. In the case of TiB₂ in an Al matrix, the TiB₂ particle surfaces form a layer of Al3Ti, which favors Al-grain nucleation due to low lattice mismatch.[115]

### 3.3. Mechanical Properties and Strengthening Mechanisms of CDAs

As shown in Table 3, the addition of ceramic particles tends to increase the elevated-temperature tensile strength of the various alloys while simultaneously reducing the elongation to failure. This tradeoff is the result of two factors. The first is particles and agglomerates cause failure initiating stress concentrations, which increase with larger particles and/or greater volume of reinforcement.[152] The second is the reduction of grain size, which limits dislocation movement and provides Hall–Petch strengthening.[153]

Strengthening mechanisms in LPBF-, LDED-, and EPBF-fabricated CDAs are the same as those manufactured via traditional methods and can be divided into either direct strengthening (continuum) or indirect strengthening (micromechanics).

In direct strengthening, the load applied on the composite is transferred from the matrix to the ceramic particles through the matrix/reinforcement interface. However, due to the particulate being nano- or microscale, direct strengthening is thought to contribute little to the overall improvement in mechanical properties.[154] However, the presence of hard ceramic particles tends to enhance wear resistance of the composite material.[155,156]

Considering indirect strengthening, there are several micromechanisms that obstruct or change dislocation motion in metals that are affected by the formation of CDAs. For elevated-temperature mechanical properties, the addition of ceramic particles mainly affects Hall–Petch strengthening and Orowan looping.

As mentioned earlier, the addition of ceramic particles to alloys can promote grain refinement (Figure 9), which results in Hall–Petch strengthening. The classic Hall–Petch equation is expressed as
where \( \sigma_{\text{yield}} \) represents the yield stress, \( \sigma_0 \) is a material constant representing the required stress to start dislocation motion, \( k \) is the Hall–Petch slope, and \( d \) is the mean grain size. \(^{[157]}\) Therefore, as grain size decreases, the Hall–Petch mechanism can contribute significantly to the overall material’s strength by restricting dislocation motion by pileups at the grain boundaries. However, there are two limitations relevant to additively fabricated CDAs exposed to elevated in-service temperatures. \(^{[158]}\) The first limitation is the presented Hall–Petch equation assumes a homogeneous grain size distribution. Therefore, one must consider part anisotropy and the conversion from columnar to equiaxed grain structure due to ceramic particle additions when quantitatively applying Equation (4) to predict strengthening. The second limitation of Equation (4) is that the effectiveness of Hall–Petch strengthening is dependent on the constants \( \sigma_0 \) and \( k \), which vary with temperature and strain.

As temperature increases, the Hall–Petch strengthening mechanism is affected due to activation of Coble (grain boundary) and/or Blum–Zeng (dislocation) creep mechanisms. Schneibel and Heilmayer\(^{[159]}\) performed a detailed analysis of the effects of these creep mechanisms on Hall–Petch strengthening of pure copper and CDA stainless steel. By modeling pure copper, the authors demonstrated that Coble creep activates at a lower temperature as grain size becomes smaller. In addition, the yield strength decline is much steeper for small grains than for larger ones. However, the strength decline from Blum–Zeng creep was not as steep as that of Coble creep even though the activation temperature was much lower. The Blum–Zeng creep activation temperature was also found to be unaffected by grain size. When CDA stainless steel was modeled and compared to observed data, it was found that the yield strength decline curve from Blum–Zeng creep fit observed data. Since the Blum–Zeng creep activation temperature is not affected by grain size, the smaller grains led to increased yield strength over the entire temperature range, even though the contribution for Hall–Petch strengthening
declined as temperature increased. This is an important advantage for LPBF fabrication, which tends to produce smaller grain sizes due to the high cooling rate.

CDAs may also experience considerable Orowan strengthening, with the strength contribution depending strongly on reinforcement particle size. Generally, the Orowan strengthening mechanism is not activated by microscale particles used as reinforcement.\[160\] In contrast, highly dispersed nanoscale reinforcement particles are effective in impeding dislocation motion and promoting dislocation multiplication via Orowan loop formation, thus increasing both elevated- and room-temperature yield strength.

Siska et al.\[161\] performed an analysis to determine strengthening from dislocation blocking and the reason for strength decrease at elevated temperature for CDA steel with Al₂O₃ or Y₂O₃ nanoparticles. By adding appropriately sized nanoscale ceramic particles, dislocation motion becomes difficult as dislocations must bypass the particles by bowing around them, forming Orowan loops. The authors described the strengthening magnitude, \(\sigma_{OR}\), as

\[
\sigma_{OR} = \frac{0.81 \text{MGb}}{r_0} \ln \left( \frac{2 \times 0.816}{\pi} \right) \frac{1 - \nu}{\lambda - 2 \times 0.816r}
\]

(5)

where \(M\) represents the Taylor factor, \(G\) the shear modulus, \(b\) the Burgers vector magnitude, \(\nu\) the Poisson's ratio, \(\lambda\) the mean planar center to the center distance between nanoclusters, \(r_0\) the dislocation core inner cutoff radius, and \(r\) the mean planar particle radius. This equation was able to describe room-temperature strengthening by Al₂O₃ reinforcement, which was much stiffer than the matrix, but overestimated strengthening by Y₂O₃ reinforcement where the stiffness was more similar to matrix. The reason for this is the stiffer particles induced a stronger stress field, trapping dislocations. As the temperature of the steel CDA increased to 600°C, dislocation cross-slip and climb easily overcame Y₂O₃ reinforcement particles, even though particle stiffness was much higher than matrix at this temperature. However, Al₂O₃ reinforcement continued to act as obstacles for mobile dislocations and allowed for dislocation trapping by Orowan loops, even though effectiveness was reduced possibly due to a combination of additional slip mechanisms and dislocation rearrangement and annihilation. It is important to note that Hall–Petch strengthening became negligible at this temperature, yet Al₂O₃ reinforcement was demonstrated to increase strength by \(\approx 29\%\) compared to oxide-free alloy. For this reason, stiff nanoscale particle reinforcements are preferable to provide increased strengthening at elevated temperatures compared to microscale particle reinforcements.

From the viewpoint of additive manufacturing, strengthening mechanisms are also influenced by the interaction of the

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Table 3. Room- and elevated-temperature mechanical properties of LPBF-fabricated ceramic dispersion alloys (CDAs).

| Material | Ceramic particle size | Volume % ceramic particles | UTS [MPa]  | Elongation,  \(\varepsilon\) [%] | Compressive yield strength [MPa] | Heat-treatment condition | Test temperature [°C] |
|----------|-----------------------|---------------------------|------------|-----------------------------|-------------------------------|---------------------------|----------------------|
| AlSi10Mg + TiCN\[111\] | No particles | No particles | 356        | 4.5  | Not tested | As-printed | RT |
|           | 2-4 μm | 2.0 | 333 | 2.8 | 270 | 4.9 | 200 |
| 316 L + TiB2\[112\] | 2–12 μm  | 5 | Not tested | Not tested | 827.5 | As-printed | RT |
|           | 10 | | | | 498.2 | 600 |
|           | | | | | 319.4 | 800 |
|           | | | | | 833.8 | 600 |
|           | | | | | 401.9 | 800 |
| 316 L + TiC\[113\] | No particles | No particles | Not tested | Not tested | 600 | As-printed | RT |
|           | 2–12 μm | 15 | | | | RT |
|           | 50 nm | | | | | |
| Al2618 + 2.3 wt% Ti 0.8 wt% B\[110\] Pre-alloyed | Pre-alloyed | 468.6 | 13.8 | Not tested | Aging | RT |
|           | 400.5 | 15.5 | 158 | 22.7 | |
| Ti–6Al–4 V + TiC\[114\] | No particles | No particles | 1078 | 4.2 | Not tested | Annealed | RT |
|           | 711 | 10.6 | 779 | 8.9 | |
|           | 200 nm | 0.5 | 1143 | 2.2 | 440⁹ | 650 |
|           | 500⁹ | 650 | |

\(\text{a)}\) Denotes values taken from a graph.
reinforcement with the laser beam and the matrix. As discussed in Section 3.1, reinforcement particles may melt partially or completely during fabrication depending on energy input and matrix and reinforcement selection. This affects strengthening mechanisms and mechanical properties. For example, when 316L reinforced with SiC is fabricated with sufficient energy density to fully melt the reinforcement, initial hardness is increased due to matrix solid solution strengthening from elemental Si and C.\textsuperscript{[162]} Full melting of reinforcement particles may also cause secondary phases to be generated, which will have different mechanical properties compared to the initial reinforcement.\textsuperscript{[163]} In the case of partial melting, an interface layer between the matrix and reinforcement is generated. If this interface is weakly bonded or brittle, the reinforcement strengthening contribution is reduced\textsuperscript{[164]}; however, in many cases, such as 316L reinforced with WC, the interface is strongly bonded to both matrix and reinforcement, and cracking is not promoted by the interface.\textsuperscript{[165]} Due to the large difference in thermal expansion coefficient that generally exists between ceramics and metals, the existence of a well-bonded interface contributes to dislocation generation near the interface, acting as an additional strengthening mechanism.\textsuperscript{[166]} This effect is expected to increase with processing temperature and may therefore be particularly strong for additively manufactured materials.

3.4. Functionally Graded Structures

The composition of CDAs alloyed ex situ is easily adjusted by controlling the quantity of ceramic powder blended with matrix powder. Furthermore, additive manufacturing processes such as LPBF, EPBF, and LDED do not require that the same powder composition is used to fabricate the entire structure, which is a significant advantage of additive manufacturing processes compared to traditional processes such as casting.\textsuperscript{[167]} Material composition can be varied along the build direction, which results in a functionally graded material (FGM) with site-specific physical properties as seen in Figure 10a. From the viewpoint of materials for use in high-temperature environments, FGMs offer an alternative to expensive secondary coatings or superalloys.

Traxel and Bandyopadhyay\textsuperscript{[168]} studied the use of LDED to fabricate graded Ti-based CDA structures by blending 5 wt% B\textsubscript{4}C or BN with commercially pure Ti metal matrix powder. B\textsubscript{4}C reacts with the Ti matrix during processing forms in situ TiC and TiB and/or TiB\textsubscript{2} reinforcement, while BN reaction with the Ti matrix forms in situ TiN and TiB. These phases have high thermal and chemical stability and increase the hardness, wear, and oxidation resistance of the composite material.\textsuperscript{[169,170]} By changing powder composition midway through the build, a functionally graded, defect-free Ti-CDA tube was fabricated with Ti-5B\textsubscript{4}C used for the lower half and Ti-5BN (wt%) for the upper half, as seen in Figure 10b. Considering physical properties, Ti without ceramic reinforcement experienced significantly higher mass gain compared to both reinforced materials during 1000 °C isothermal oxidation test in air as seen in Figure 10c, indicating ceramic reinforcement reduced scale growth. Even though oxidation resistance for both reinforced materials was similar, significant hardness differences existed. Hardness of Ti reinforced with 5 wt% BN demonstrated hardness of 713 and 920 HV\textsubscript{0.2/15} in the

Figure 10. a) Overview of LDED fabrication of functionally graded material (FGM); b) example of Ti and Ti-5B\textsubscript{4}C to Ti-5BN (wt%) FGM structures; c) isothermal-oxidation weight change curves for Ti, Ti-5B\textsubscript{4}C, Ti-5BN, and Ti-2.5B\textsubscript{4}C-2.5BN (wt%). Reproduced with permission.\textsuperscript{[168]} Copyright 2020, Elsevier.
as-printed condition and after the 1000 °C isothermal oxidation test, respectively, while hardness of Ti reinforced with 5 wt% B$_{3}$C was 348 and 465 HV$_{0.2/15}$ in the as-printed condition and after the 1000 °C isothermal oxidation test, respectively. Unreinforced Ti hardness was 274 and 322 HV$_{0.2/15}$ in the as-printed condition and after the 1000 °C isothermal oxidation test, respectively.

Comparing LPBF, EPBF, and LDED for FGM manufacturing suitability, it is apparent that powder bed processes are currently not as flexible as LDED. Fabrication of FGM with powder bed processes requires changing the powder bed when it is necessary to alter composition since current machines do not have a provision for multi-material storage or blending. However, custom-fabricated technical solutions have been successfully demonstrated.[171] In comparison, LDED may be fitted with separate powder feeders and a dosing mechanism to blend and supply powder to the LDED nozzle, allowing for a continuous gradient from material A to material B or even material C during fabrication.[172,173]

4. Current Challenges and Future Research Directions

Additive manufacturing is a complex process and understanding it requires knowledge of metallurgy, chemistry, and complex heat flow, making it necessary for a multidisciplinary approach to optimize processing parameters and alloy compositions to eliminate defects and achieve desired mechanical properties. Additive manufacturing enables unique mechanical properties to be achieved in ICs, such as LPBF-fabricated TiAl$_{22}$Nb$_{25}$, which demonstrates exceptional room-temperature ductility in the as-printed state due to matrix supersaturation and a small quantity and fine distribution of secondary phase. However, heat treatment is required to precipitate phases necessary for high-temperature strength retention, and room-temperature ductility suffers as a result. Cracking in ICs is a significant issue that may make a material unsuitable for certain additive manufacturing processes. For example, EPBF build-platform heating temperature is above DBTT of TiAl alloys, reducing cracking propensity during fabrication relative to LPBF and LDED. However, this brings a tradeoff in the form of microstructure evolution due to in situ heat treatment with EPBF, which is avoided for LPBF and LDED since these processes do not require build-platform heating.

With ex situ CDAs, the laser absorption of reinforcement may be significantly higher or lower compared to the matrix; however, electron-beam heating of ceramic reinforcement is generally lower due to the lower electrical conductivity relative to matrix. Higher laser absorptivity of reinforcements may contribute to partial or complete melting of the reinforcement phase, with effects on porosity, mechanical properties, and strengthening mechanisms dependent on the matrix and reinforcement. In the case of LDED-fabricated 316 L reinforced with WC, a reaction occurs that leads to interfacial layer formation and strong reinforcement bonding to the matrix. Retention of a solid reinforcement phase during material processing allows for grain refinement and Orowan strengthening mechanisms to increase the elevated-temperature mechanical properties. However, reinforcements remaining in the solid state during matrix melting also cause an increase in melt viscosity, potentially leading to porosity formation.

High-level challenges for IC- and CDA-additive manufacturing are as follows: 1) LPBF and LDED are difficult to apply to many NiAl-, TiAl-, and FeAl-based ICs due to cracking. The high cracking propensity is due to several factors, including inherent low ductility and poor fracture toughness, grain boundary and/or bulk material hydrogen embrittlement, steep thermal gradients during fabrication causing high stress due to localized material contraction, and solidification cracking due to presence of thin liquid film during the final stages of solidification that cannot accommodate solidification contraction. Steps to reduce cracking propensity include processing parameter control and appropriate alloying element selection. 2) CDAs may suffer from porosity due to high melt viscosity. The cause for this is the reinforcement particles being present as a solid in the melt during fabrication, and control of this phenomenon requires careful selection of matrix, reinforcement, and quantity of added reinforcement to prevent excessive melt viscosity. Increasing melt temperature through processing parameter control may also reduce melt viscosity and prevent porosity formation; however, excessive heat input can also melt the reinforcement and change the strengthening mechanisms.

Additive manufacturing technologies offer great opportunities for the development of the next generation of components for power generation, transportation and aerospace engines, spacecraft, and other applications with high in-service temperatures. ICs provide excellent elevated-temperature mechanical property retention, making them useful for in-service temperatures of up to 900 °C or more depending on the alloy. Meanwhile, CDAs fill an economic and technological gap for structural materials with service temperatures of around 250–600 °C depending on the matrix and reinforcement, while simultaneously providing enhanced wear resistance. Potential research directions are highlighted as follows: 1) ICs are likely to find use in corrosive environments and in applications that are sensitive to creep, such as in the hot section of a jet engine turbine. Therefore, extensive research on enhancing elevated-temperature mechanical properties and strengthening mechanisms should be conducted to identify areas of potential improvement. For example, due to the high cooling rates during additive manufacturing, the formation of columnar grains is often promoted. In the case of high-temperature capable superalloys, it has been demonstrated that directional solidification enables significant improvements to mechanical properties due to the reduced number of transverse grain boundaries.[174] Beneficial effects include longer cyclical strain life and reduced creep; however, this phenomenon has not been investigated in depth for additively manufactured ICs where directional solidification naturally occurs but is not readily achieved by other manufacturing methods. 2) Cracking suppression in ICs is achieved through process control and alloying. However, insufficient knowledge exists on the impact of alloying on material properties from the viewpoint of additive manufacturing. For example, addition of Ti and B to FeAl ICs lowers the DBTT, and this effect depends on the processing method and sample orientation during testing. For cast Fe–30Al–5Ti–0.7B, samples become fully ductile at 650 °C, while this occurs for LPBF samples at 300 °C when tested vertical to the build direction and at 450 °C when tested parallel to the build.
direction. For LDED samples, full ductility is achieved between 500 and 550 °C for both testing orientations. Considering microstructure, obvious differences are apparent between fabrication methods. Fe–30Al–5Ti–0.7B fabricated by LPBF or LDED forms TiB$_2$ at L2$_1$ grain boundaries and within grains, while Fe–28Al–5Ti–1.3B fabricated through EPBF only forms TiB$_2$ at matrix grain boundaries. These differences are caused by fundamentally different processing characteristics resulting in different melt pool sizes, cooling rates, thermal gradients, maximum melt temperature, etc. The impact of different processing methods as well as changes to individual processing parameters has not yet been widely investigated, creating a significant knowledge gap. 3) Considering CDAs, research has mostly focused on parameter optimization, defect elimination, and room-temperature mechanical properties, yet relatively few studies exist on elevated-temperature mechanical property characterization and improvement, especially for fabrication methods other than LPBF. Furthermore, we are at the early stages of alloy development specifically for additive manufacturing processes and CDAs may play a major role in the future of additive manufacturing due the ceramic particles acting as heterogeneous nucleation sites during solidification, causing reduction or elimination of solidification cracking and reduction of anisotropy for difficult to manufacture alloys. 4) The combination of metal matrix and reinforcement provides a potentially low-cost method of tailoring microstructure and properties through ceramic addition control. Furthermore, it is not necessary to use a single material composition for the entire part. Many different variant compositions can be created through powder blending, which can then be used to fabricate structures with mechanical and/or thermal properties varying along the build direction, thus achieving site-specific functionality. However, this requires understanding of required processing parameters for each composition to achieve high densification and expected properties for each zone. 5) For both ICs and CDAs, reduction in post-processing requirements is an advantage compared to traditional fabrication when considering manufacturing cost and time. ICs are difficult or impossible to machine; therefore, additive manufacturing is appealing, especially from the view of design optimization. Even though it may be possible to fabricate cube samples, it is not always possible to fabricate complex geometries with the same material and processing due to generation of cracks in thin structures, warping, and low overhang angle limits. Additional research on factors affecting complex structure processability for relevant applications, such as turbine blades with integrated cooling passages, will be beneficial in bringing new materials from the development stage to commercial use. 6) Additive manufacturing in general has been positively influenced by the use of artificial intelligence and the development of numerical models. These tools can be used to predict or visualize important factors during additive manufacturing, such as thermal gradients, microstructure development, or melt pool dynamics. Therefore, a comprehensive understanding of the intricate mechanisms behind additive manufacturing is provided, allowing for process optimization. It is likely that the future of ICs and CDAs will be heavily influenced by advanced digital data analysis and methodology such as in situ process monitoring, big-data statistics, and digital twins.

5. Summary

LPBF, LDED, and EPBF are additive fabrication methods that lead to unique microstructures and mechanical properties while also reducing or eliminating the need for part post-processing. By applying additive technologies to ICs, which cannot be easily formed or machined but are particularly suited for use at elevated temperatures due to high elevated-temperature-specific strength, the use of these materials in industry can be expanded. Meanwhile, the addition of ceramic particles to crack-sensitive alloys enables defect-free additive fabrication. Therefore, CDAs, which are also suitable for use in elevated-temperature applications, expand the available materials pallet and may play a large role in the future of additive manufactured materials. This work examined the recent advances in LPBF, LDED, and EPBF of ICs and CDAs to understand strengthening mechanisms and the effects of material composition and specific fabrication operations on microstructure and mechanical property development. Defect formation mechanisms were also discussed, and attention was directed toward high-temperature applications. Based on the reviewed information, suggestions for future research were also provided.

Acknowledgements

X.P.L. would like to acknowledge the financial support from Australian Research Council (ARC) Discovery Early Career Researcher Award (DECRA) DE190101495.

Open access publishing facilitated by University of New South Wales, as part of the Wiley - University of New South Wales agreement via the Council of Australian University Librarians.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

additive manufacturing, ceramic dispersion alloys, high temperature materials, intermetallic compounds, laser processing

Received: January 30, 2022
Revised: March 14, 2022
Published online: March 31, 2022

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