Embedding Function within Additively Manufactured Parts: Materials Challenges and Opportunities

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As additive manufacturing (AM), particularly metal and polymer-based 3D printing, progresses from a scientific curiosity to an industry mainstay, there is an increasing desire for parts to take on secondary roles beyond their primary, typically structural or mechanical, function. This may enable unique and broadranging functional customization, including monitoring part performance or its local environment, provisions for unique identifiers in tracking, anticounterfeiting, quality control, and even product certification. Many materials and processing compatibility requirements must be addressed to achieve embedded function, as embedded fillers or additives must not compromise either the part's production or its primary function. Herein, the material, technological, and processing challenges are highlighted for embedding function into parts produced by some of the most popular AM techniques, with examples provided from the literature. While it is possible to produce cavities within 3D printed parts and place functional components within them postbuild, approaches, herein, specifically explore direct incorporation of functional agents, fillers, and additives during the build process that imparts ancillary function. It is hoped to inspire exploration of the possibilities and enhancements achievable through functional AM. On account of its versatility, binder jetting is analyzed as a case study, with novel approaches for embedding new functions outlined.

1. Introduction

Additive manufacturing, AM, aka 3D printing, is particularly attractive as it enables the production of bespoke parts with almost complete geometric freedom, no longer bound by many of the constraints in traditional manufacturing approaches. Since its advent, AM has stimulated enormous interest; however, much of the research has centered on material and process optimization for producing "high-quality" parts whose mechanical properties and performance can match those of their traditionally manufactured counterparts.

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The unique build-up mechanisms in AM offer greater possibilities than just geometric and design freedom. One such possibility is embedded function, which can add value and capability beyond the component's primary function. Embedding function within an AM part refers to the control of (micro-)structural features or to the inclusion of materials or components that are incorporated within the part, and which provide the part with ancillary functions beyond its primary, often structural or mechanical, function.

If, for example, an AM impeller is considered, then its primary purpose is to increase the pressure and flow of a fluid. However, if devices were incorporated during its manufacture to enable sensing of temperature and strain, then these would provide the impeller with secondary (monitoring) functions beyond its primary (mechanical) role. It is not just sensors or discrete elements at the macroscale which can impart function, but also elements at the microscale. If considering the case of an AM static mixer, its primary function

is to ensure uniform mixing across its length, yet if catalytic elements are distributed at specific locations within the mixer, then its secondary function would be to increase the rate at which chemical reactions take place between reactants passing through.

Imparting an embedded sensing capability is highly attractive and can serve broad-ranging applications including monitoring the part's performance, lifetime, and environment. However, a whole host of embedded functions are possible other than sensing. Advanced ancillary features may serve as unique identifying codes for quality assurance (QA) or product identification.^[1] As discussed in the following sections, embedded fillers and additives may also function as receptors for facilitating signal communication to the printed part or provide information on the success/failure of a build process. Others may entail enhancing mechanical properties of parts by improving densification or consolidation upon printing, and even provide a smoother surface finish or increase wear resistance. The inclusion of corrosion inhibition molecules may also be explored to improve the corrosion resistance.

There are a multitude of possibilities for embedding function into AM parts, and the emerging strategies for functionalization could be applied broadly within the AM space, in materials and systems ranging from metals to ceramics, from polymers to textiles. However, there are also a multitude of technological

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challenges that must be addressed on a case-by-case basis in order to achieve embedded function. In this regard, the AM technique utilized for part production is critical, with certain AM techniques being more suitable than others, depending on the materials involved, the required processing conditions, and the part's intended application. These factors—material compatibility, utilized technique, pre- and postprocessing—must all be diligently considered when attempting to develop AM parts with embedded function.

This article is intended to provide the reader with a high-level overview that outlines a number of concepts for embedding functional components into 3D printed parts while taking into account the key materials and processing challenges for each AM technique. Although there are a great number of AM technologies available, herein we focus on a selected few which are mainstream in research and industry, and which are more conducive for incorporating an embedded function. Furthermore, approaches that involve placing components or electronic devices within cavities of the 3D printed part are not considered, as our primary objective is to outline embedded systems that are manufactured together and become integral with the printed part.

2. Key Considerations

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When determining viable approaches for embedding function, a number of key physical and chemical requirements must be considered. The principal technological challenges are compatibility of the functional agents (fillers, additives) with the matrix they are being embedded into, as well as compatibility with the processing conditions. This needs to be considered both during the build and in any postbuild processing. The functional materials must possess a means for being integrated into the bulk material, being able to chemically or physically bind to the bulk.

While chemical compatibility is extremely important, it is also necessary to ensure that the introduced functional agents do not negatively affect the mechanical properties and do not result in any reduction in performance or intended function of the bulk, i.e., induce corrosion, fatigue, loss of mechanical and structural performance, decrease in biocompatibility, etc. An example of these potential side effects could be the junction or boundary of two dissimilar metals in a part that results in unintended galvanic corrosion, especially if they are at locations where they may be exposed to moisture.

The functional agents which are embedded in the part during the build must not interfere with the AM process. Meanwhile, they must be capable of withstanding the chemical reactions and the temperatures encountered in the process, including any postbuild processing, in order for them to retain their function. There may be an exception to this, if, for example, the embedded material's function is to leave pores/voids in the part when subjected to higher temperatures. It may also be the case that the embedded function is realized only upon heat treatment, where heating and cooling may drive a reaction of the functional agents to completion.

Although the term "multimaterial" is often employed in the literature to denote any object consisting of two or more materials,^[2–4] for a matter of clarity the term "multimaterial" is applied here to mean that discrete areas made of different materials coexist in the same object, while "composite" is a

material that combines two (or more) components having different properties and distinct boundaries, oftentimes featuring a filler (which can be a functional agent, or a reinforcement, or even an inexpensive extender) dispersed in a continuous matrix.

Many of these key considerations are both technique- and application-specific, and will be exemplified in further detail in subsequent sections.

3. AM Techniques and Embedding Function into Parts Made by Them

While many AM techniques exist, herein we highlight a few of those most commonly utilized by research and industry. Each paragraph begins with a brief introduction to the AM technique, followed by an overview of the main material and processing challenges while citing some relevant examples from the literature where applicable.

3.1. Powder Bed Fusion

Powder bed fusion (PBF) covers a variety of techniques, including selective laser sintering/melting (SLS/SLM) and electron beam melting (EBM). An energy source such as a laser or electron beam is directed toward a uniform layer of powder, where it is scanned to generate a cross section of the part, fusing the powder in the process. Once the layer is complete, the build plate containing the powder bed is lowered by an amount corresponding to one layer thickness, a new layer of powder is raked over the bed, and the laser or electron beam once again scanned on the powder bed to generate the part's subsequent cross section and fuse it to the previous layer. The process is repeated until the part has been completed. Part's consolidation may be achieved either by sintering (SLS) or by melting (SLM and EBM). In terms of feedstock materials, SLS mainly refers to PBF as applied to thermoplastic-based powders, while SLM preferentially works with metal-based powders (a detailed discussion of the different consolidation mechanisms was outlined by Kruth et al.^[5]). Direct metal laser sintering (DMLS) is a sort of compromise, as it works with metals like SLM, but parts are consolidated through sintering, rather than melting, which is typical of SLS. Only conductive materials can be processed by EBM, which limits the technique to processing metals and few conductive ceramics.^[6] An illustration of working principle of PFB is schematized in Figure 1.

Regardless of the specific technology in use, much attention in the literature has been paid to embedding functionality through the development of new materials, including alloys and composites, rather than part comprised of multimaterial systems. Generally speaking, multimaterial printing by PBF is still in its infancy,^[7] likely because it requires complicated procedures (e.g., the deposition, consolidation, and cleaning of alternating powders' layers^[8]) or extensive hardware customization.^[9] Also, multimaterial printing may potentially cause bonding issues at the interface between dissimilar materials, thermal stresses due to the thermodilatometric mismatch, and, in metal-based systems, galvanic corrosion in service, should the materials be bridged by an electrolyte. An additional concern comes from the difficulty of recycling and ultimately disposing of mixed exhausted powders.





Figure 1. Illustration of powder bed fusion techniques, where an energy source (laser beam, electron beam) is scanned over a successively deposited layers of powder forming the part.

3.1.1. SLS

At present, just a few thermoplastic materials are routinely 3D printed by SLS to obtain parts with minimal residual porosity and with high resolution and dimensional accuracy. Among them, polyamide is the preferred choice due to its ability to produce highly dense objects with appreciable mechanical strength.^[10] To deliver SLS parts with a wider range of functionalities, new materials are being developed, and existing ones are being modified.^[11] Two (or more) different polymers can also be blended in order to take advantage of the properties of both.^[12,13] Several approaches have been proposed in the literature to add fillers and additives in SLS.^[14] **Figure 2** shows some examples of different powders resulting in composite parts.

One approach consists of producing composite pellets prior to printing by SLS. This method has been demonstrated, for example, by Li et al.^[15] who synthetized in situ grown nanohydroxyapatite hybridized graphene oxide and added it to an ethanol solution of a 1:1 mixture of poly(lactic acid) (PLA) and polycaprolactone (PCL). Then the dispersion was treated by centrifugal washing and vacuum drying to obtain a composite powder. Ultimately, the composite scaffolds printed by SLS exhibited increased strength and bioactivity as compared to neat PLA scaffolds.^[15] Instead of being homogenously dispersed in the polymer matrix, the filler particles can be coated with a polymer film. Zhu et al.^[16] successfully prepared polyamide 12 (PA12)-coated carbon fibers having this core-shell structure by a dissolution-precipitation method. Interestingly, upon printing, the PA12 shell acted like a glue to keep the carbon fibers together. Taking advantage of the abundant residual porosity. the SLS composite parts were subsequently infiltrated with epoxy resin for increased tensile and flexural strength. The opposite route has also been attempted, where the polymer particles receive the filler as a surface coating. The filler on the surface of the polymer particles usually survives into the 3D part as a segregated network, which is particularly advantageous to lower the percolation threshold in electrically conductive composite parts.^[17,18] A simple blend of filler particles and polymer pellets can also be used as feedstock, which has also been demonstrated with multiphase systems.^[19] However, this may result in flowability issues or powder segregation. These problems become particularly serious when processing inorganic fillers, like ceramics or, even worse, metals, whose density is typically much higher than that of thermoplastics, with some exceptions such as hollow glass spheres.^[20] As polymer sintering does not need high temperatures, the process is compatible with a wide range of fillers and additives, provided they are not extremely heat-sensitive. However, fillers and additives should not change the feedstock powder flowability, which is crucial to rack very



Figure 2. Composite parts can be produced by SLS starting from different feedstock powders: composite particles, where the filler and the polymer matrix have been compounded before printing, typically leading to composites with homogenous filler distribution; polymer particles that have been precoated with filler particles, typically leading to segregated structures; and from filler particles that have been precoated with polymer typically leading to homogeneous composites with some degree of residual porosity.

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thin and homogeneous powder layers.^[21] Further, although fillers and additives inevitably require some adjustment of the processing parameters, they should not compromise the laserinduced consolidation processes.^[22] Quite often, fillers act as nucleating agents that promote the crystallization of semicrystalline thermoplastics, which may affect the properties of the printed part, as well as reduce the processing window.^[23]

3.1.2. SLM

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Embedding function in SLM typically entails preparing alloys or metal matrix composites.

Two main routes have been attempted to produce composite parts by SLM. The first is the ex situ approach, where functional particles are added to the metal powder before printing. The basic requirement is that the functional particles do not melt during processing, nor react with the matrix, so that they remain unaltered into the finished part. The second is the insitu approach, where primary particles melt completely upon processing and reprecipitate or react to produce new functional particles. Theoretically, the main advantage of the exsitu method is the wide variety of particles that can be incorporated, even with a complicated chemistry. However, decomposition, melting, and reaction phenomena are frequently reported^[24-26] and in practice just a few compounds, mainly in the carbide and nitride families, are so thermally and chemically stable as to survive the laser melting process.^[27] As a result of the in situ method, functional particles are usually well distributed within the matrix. Also, secondary particles have contaminant-free surfaces, and this is expected to improve their bonding to the metal matrix. However, secondary particles generally have a very simple chemical composition, as it is extremely difficult to target a complicated compound through remelting and/or chemical reactions with the metal matrix.^[28] In spite of the increasing attention being paid to SLM of metal matrix composites, many hurdles remain. Quite often, the behavior of new materials, especially ceramics, under the laser beam is unpredictable, due to the lack of preexisting reference data. The presence of a second material is likely to alter the melt rheology of the metal matrix causing disrupted Marangoni convection and high viscosity. For exsitu composites, molten metals have poor surface wettability to oxides and to impurities, which undermines the strength of the matrix-filler interface.^[29] Also, microsegregation is likely to occur. This problem may persist even when core-shell composite powders are processed instead of powder blends.^[30] According to Gu et al.,^[31] the laser energy is a key parameter in this regard because for low values of the energy density the weak Marangoni convection is insufficient to redistribute the filler particles in the melt pool, which is likely to result in particle aggregation and uneven distribution, whereas for higher values of the energy density the Marangoni convection, combined with repulsive forces, pushes the particles back around the melt pool to form ring-like structures which are deemed responsible for grain refinement and grain boundary strengthening. This ring-like arrangement has been observed for both nonoxide^[31] and oxide fillers.^[32] In particular, nanosized fillers have a strong tendency to agglomerate due to their high specific surface area. Fine particles may also impair the powder flowability due to strong van der Waals forces.^[33] Another difficulty comes from the specificity of the processing conditions that must be individually tuned for each composite as a function of the constituent phases, volume fractions, and characteristics (size, shape) of the feedstock powders in use.^[25]

Likewise, alloying can be accomplished either ex situ or in situ. Although printing from prealloyed powders may be a straightforward approach to achieve this, in situ alloying offers several advantages in order to respond to the increasing demand for new materials in SLM. On the one hand, test compositions can be easily modified, enabling fast completion of feasibility studies of different alloy compositions. On the other hand, after adjusting the processing parameters, in situ alloyed parts achieve comparable properties to those produced from prealloyed powders, but at a reduced cost, because standard metal powders are on average more affordable than bespoke prealloyed feedstocks.^[34]

3.1.3. EBM

In EBM, similarly to SLM, new functions can be provided by the addition of fillers to obtain composite parts. This can be done by preblending the filler and the metal powder before printing according to the ex situ approach.^[35] Alternatively, multiphase systems can also be achieved in situ by inducing controlled precipitation phenomena and reactions starting from prealloyed powders.^[36]

With respect to SLM, EBM is compatible with a rather narrow range of electrically conductive materials, which mainly include alloys, and a few metals such as pure titanium (popular because of its biomedical applications), pure copper (because of its thermal and electrical conductivity), and pure niobium (because of its superconductivity).^[37] Caution must also be taken, for unlike SLM, the EBM build chamber is held under vacuum, hence the saturation vapor pressure of any material being introduced must be carefully considered so that it does not vaporize and hence is compatible with the process. Moreover, the identification of appropriate processing parameters for new materials often requires extensive research and incurs substantial costs. This limits the drive for exploring new feedstocks in EBM.^[38] However, EBM offers a wide spectrum of processing parameters and enables the site-specific control of the crystallographic orientation in metal parts. As a consequence, new functionality can be embedded in printed parts through the artful manipulation of the grain structure of existing printable materials, which may represent a profitable alternative to developing novel materials.[39]

3.2. Direct(ed) Energy Deposition

Also known by names such as direct metal deposition (DMD), laser engineered net shaping (LENS), electron beam additive manufacturing (EBAM), etc., direct(ed) energy deposition (DED) is a metal AM technique whereby feedstock material is pushed through a nozzle, after which it is immediately melted by an energy source and deposited onto a target surface where it subsequently solidifies. The system can be considered akin to a welding apparatus placed on a robotic arm.^[40] The feedstock



material is typically a metal or alloy powder, and the energy source is normally a high intensity laser or electron beam, or sometimes a plasma/electric arc. The printhead is generally mounted onto a multiaxis robotic arm that enables a wide range of geometries to be printed.^[41] A more recent addition to the DED family is wire arc additive manufacturing (WAAM), where a metal wire is used instead of a powder, and a variety of power sources can be used to drive the arc deposition process.^[42] DED systems are capable of depositing material at high rates, especially if the feedstock is in wire form.^[43] Although free-standing parts can also be obtained by DED, the main application for this technique is repairing or adding material to existing objects.^[44] The resolution in DED is typically lower than in PBF, especially SLM, and parts often require postprocessing. However, modern hybrid equipment combines DED and computer numerical controlled (CNC) machining for a very precise finishing of complicated geometries.^[45] An example of the process can be seen in Figure 3.

Owing to its versatility, DED has been successfully explored for printing a wide range of metals and alloys, as well as metal-matrix composites.^[43] Research is growing to determine the printability of new materials, like intermetallics, shape memory alloys and high entropy alloys, and even ceramics.^[46] DED techniques have the benefit of being equipped with multiple hoppers/powder feeders that potentially allow different materials to be deposited interchangeably, such as at specific sites within the build. Otherwise, the simultaneous input and melting of different powders in the same melt pool enable the in situ synthesis of metal alloys, whose composition may be changed point-bypoint.^[40] However, the prevalent application of DED is currently in depositing bimetallic structures and functionally graded materials (FGMs), both of which combine different materials in the same object in order to deliver different functions in different locations^{.[47]} As compared to bimetallic structures, FGMs feature a gradual change in composition that helps reduce residual stresses and solidification cracking.^[47] If properly designed, the compositional change may also reduce the formation of brittle intermetallics.^[48] Powder-fed systems are usually preferred to wire-fed ones for producing FGMs, owing to the relatively easy input of different powders into the melt pool.^[49] However, wirefed DED has also been demonstrated for producing FGMs.^[50]

Besides FGMs, multilayered structures that combine and alternate strata of different metals in the same object are feasible by DED, although the stacking accuracy is lower than in emerging multimaterials PBF systems.^[47]

3.3. Material Extrusion by Fused Filament Fabrication

By far one the most popular material extrusion (MEX) techniques among industry and hobbyists, and commonly known by the trademarked name fused deposition modeling (FDM), fused filament fabrication (FFF) works by heating, melting, and extruding a thermoplastic-based filament through a heated nozzle, where it forms a paste that is then used to effectively draw the cross-sectional shape of a part that is built up layer-by-layer. While there are numerous equipment configurations, the most common have a printhead mounted on an *x*, *y* stage that prints the cross section onto the build plate, and once the layer is completely drawn, the build plate lowers and the subsequent layer is printed over the previous one.^[51,52] A typical FFF printing process is illustrated in **Figure 4**.

One of the advantages of FFF is the ability to simultaneously print two (sometimes more) materials through separate nozzles. The easiest way to embed new functionality is thus to combine two (or more) different materials in the same object, in order to provide the required properties at different locations.^[53] However, this method is only feasible when working with a dual (or multi-) nozzle printing hardware. Otherwise, the job must be interrupted to allow the operator to switch the filament, and then resumed, which substantially increases the printing time and complexity.

A different approach to embedding functionality comes from the shift from neat thermoplastics to composite filaments.^[54] As opposed to the greatest part of AM methods, FFF is compatible with a potentially endless range of composites, including continuous fiber-reinforced ones (although printing continuous fibers does require dedicated equipment^[55,56]). In principle, the coexistence of several fillers in the same filament may also activate



Figure 3. A DED system, in which the powders emanate from the print head, along with an energy beam (laser, electron, etc.), which melts them onto the build platform and previously deposited layers. Multiple feed-stocks can be utilized, each feeding the printhead from separate hoppers.



Figure 4. Illustration of a FFF printer, where different filaments can be fed into the print head that moves on an x, y gantry. The printhead extrudes the filaments through separate nozzles, depositing them onto the build platform in a layer-by-layer fashion.

multiple functions at the same time. Otherwise, individual fillers that are intrinsically multifunctional may impart several properties at once. This is the case, for example, of continuous carbon fibers. Mainly explored as structural reinforcement (increased stiffness and tensile strength), continuous carbon fibers exhibit a piezoresistive behavior that can be leveraged to impart self-sensing capabilities to the printed part because the conduction of electricity along the fibers is sensitive to applied loads and to structural damages.^[57] In the "shaping, debinding, and sintering" (SDS) process, aka fused deposition of ceramics and fused deposition of metals, filaments contain an extremely high filler loading, typically exceeding 55-60 wt%, and the polymer matrix works as a temporary binder to glue the inorganic particles together while printing. After printing, the polymer matrix is removed, and the green part sintered into a fully inorganic object. This offers the exciting possibility of producing parts with new properties, substantially different from those of conventional FFF parts).^[58-61] However, incorporating one or more fillers inevitably changes the printability of the polymer matrix, with technical challenges that should be considered on a case-by-case basis according to the nature of the filler(s) and the matrix, and according to their relative amounts.^[62] Also, some fillers, especially vegetable fibers,^[63] may be incompatible with the temperatures required for printing standard polymers, such as PLA and acrylonitrile-butadiene-styrene (ABS), that become

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While the most common way of printing composite materials by FFF relies on achieving a homogenous distribution of the filler within the polymer matrix, alternatively the filler can be selectively distributed where it is required for fulfilling a specific function. For example, the presence of carbon nanotubes on the filament's surface can survive through the printhead and induce a local enrichment that is responsible for improved part's consolidation and for the early establishment of the percolation threshold for electrical conductivity.^[64]

processable in the 180-240 °C range.

Besides developing new polymers for FFF (including thermoset polymers featuring reversible covalent bonding^[65,66]), blending different polymers, or extruding core-shell multipolymer filaments may also provide ancillary functionality. For example, filaments having an outer shell made of either low-density (LDPE) or high-density polyethylene (HDPE) on a polycarbonate (PC)/ABS blend core provide higher impact resistance, and enhanced elongation at break as compared to PC/ABS alone. Interestingly, it has been reported that using LDPE instead of HDPE significantly improves the printing accuracy, but also reduces the elastic modulus of the printed parts.^[67] Filaments for 3D pharming, which is the AM of personalized tablets and drug delivery systems, can be soaked in a water-based solution of the required active principle. This makes it possible to load the filament (especially its surface) while avoiding the hot-melt extrusion of thermally labile substances.^[68]

Although objects produced by FFF always retain some residual porosity,^[69] postprinting infiltration is not standard practice. However, printed parts may be treated to receive a functional coating as demonstrated, for example, by Sevastaki et al.,^[70] who 3D printed PLA scaffolds with a high specific surface area and coated them with ZnO to induce the degradation of paracetamol, a medicine that, due to its popularity, is often held responsible for water pollution.

3.4. Vat Photopolymerization by Stereolithography

Stereolithography, often referred to as stereolithographic apparatus (SLA), is the most popular technique of the vat photopolymerization (VPP) family, aka resin 3D printing. A light source, which can be a laser beam or projector in digital light processing (DLP), is directed toward a vat containing a photocurable polymer. The impinging light cures the polymer, solidifying it.

Two hardware configurations are feasible in SLA, often referred to as "bottom-up" and "top-down" configurations (however, it is worth noting that the literature is not consistent in using this terminology, with the two names being often inverted-see, e.g., the contribution by Moritz and Maleksaeedi^[71] as opposed to the contribution by Voet et al).^[72] In the bottom-up configuration, which is typical of desktop printers, the light source sits below the resin tank, while the build platform is located above the resin tank. In this configuration, the build platform moves upward and gradually pulls the part out from the resin bath. The bottom of the vat must be transparent to the light beam and must be kept perfectly clean of any undesired hardened material bits. In the top-down configuration, which is instead typical of industrial printers, the light source sits above the vat. The build platform, which is completely immersed in the resin bath, moves downward, and drags down the part. Printing is faster in the top-down configuration than in the bottom-up one. However, the vat must be large enough to contain the build platform and the whole part, which usually necessitates substantial volumes of resin. While classical SLA systems scan a single light beam to trace a layer, and then the process is repeated layer upon layer, as mentioned above in DLP the light is projected to cure the whole layer at once, thus reducing the printing time. Regardless of the specific equipment in use, SLA parts need postprocessing, as any excess resin must be washed off and oftentimes curing reactions must be completed in a UV oven (postcuring). An example of a bottom-up SLA configuration is shown in Figure 5.

Although normal SLA equipment is limited to process only one material at a time, various attempts have been made to print multimaterial parts. Traditionally, the change in printing material has been accomplished by removing the part from the resin bath, washing, and then resuming the printing job in a second resin bath. Recently, dynamic fluidic control has enabled more



Figure 5. A bottom-up SLA system showing the light source directed through the vat of resin, where mirrors direct the beam onto the build plate, curing the resin in the process. As the build platform is raised, a new layer of polymer is cured by the light beam in the desired pattern.

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efficient avenues to changing material upon printing. Multimaterial printing with a single vat has also been demonstrated with resin–resin mixtures, where each resin is curable under a different wavelength. Schmidleithner et al.,^[73] for example, combined a resin printable under blue light through free radical reaction, and a resin printable under UV light through a ring-opening cationic reaction. Printing required two separate.STL files, one for each resin, to control the action of the two different light sources and locally cure either material.

Grayscale printing applies different illumination conditions, corresponding to different light intensity values, in different points of a layer. The degree of curing decreases with the increasing gravscale percentage and this enables the obtainment of functional gradients. However, the underexposed areas often suffer from weak mechanical properties. Also, potentially toxic unreacted monomers may survive into the printed part. Kuang et al.^[74] proposed to avoid these issues through a two-stage process, where the first curing step by grayscale light printing was followed by a second-stage thermal curing to improve the functional gradient and eliminate most of the residual monomers. The finished parts exhibited a multifunctional gradient, meaning that not only the mechanical properties, but also the thermal properties (glass transition temperature) and the diffusivity were position-dependent. The diffusivity pattern was leveraged to develop a new encryption method through diffusion-assisted coloring.^[74]

Powder-filled composites can be printed by SLA, and, similar to FFF, fully inorganic objects can also be obtained after removing the polymer matrix, generally by thermal debinding. However, printing composites by SLA present some technical challenges. First, the presence of the filler can drastically reduce the shelf life of the resin due to precipitation phenomena, and vigorous shaking may be required to restore an even distribution. Strong agglomeration phenomena are expected when working with nanometersized fillers. Second, depending on the particle size distribution of the filler and on the refractive index of the filler and the resin, particles may cause scattering of the impinging light, thus undermining the performance of the printer in terms of curing effi-ciency and printing accuracy.^[75,76] Both issues are worsened when high filler loadings are required, such as for producing fully inorganic parts.^[77,78] Alternatively, fully ceramic objects can be obtained from preceramic photocurable polymers, which consist of an inorganic backbone modified with photoactive groups. After printing, the backbone can be converted into a ceramic material by pyrolysis under inert atmosphere.^[79] As all components are dissolved in liquid solution, working with ceramic precursors avoids light scattering. However, the range of obtainable materials is somewhat limited to SiOC, SiC, SiCN, Si₃N₄, boron nitride, and aluminum nitride ceramics.^[75] Some preliminary attempts have been made to embed fabrics as a reinforcement, but this usually requires a multistep process, because the printing job must be interrupted, the fabric must be impregnated into the resin bath and manually applied onto the printed layers, and ultimately the printing process must be resumed to completion.^[80]

3.5. Binder Jetting

Binder jetting (BJT) is an AM technique in which a thin layer of powder is distributed over a build platform, after which a

printhead deposits a chemical adhesive over selected areas of the powder. Following this, a fresh layer of powder is raked over the build platform and bonds to the adhesive layer beneath it. The process is then repeated, and the part is built up layer-by-layer. Typically, a two-part binder system is utilized to consolidate the part, with the feedstock powder being precoated with one part of the binder system, and the second part being delivered through the printhead during jetting. This process is illustrated in **Figure 6**.

A host of powder materials can be used in jetting techniques, from sand, metals, ceramics, and polymers. Besides the versatility to treat a variety of feedstock materials, advantages of such binder jet systems over laser PBF and DED include the capacity for printing at room or lower temperatures, as well as the ability to produce significantly larger builds. In many cases, posttreatment may be required following the build. This may be either to aid in the curing of the binder, or to sinter the final product and render it fit for service. Builds may also require infiltration with smaller particles to decrease their porosity. The common binders for binder jetting include: 1) Furan binder, which is a typical nobake binder found in traditional sand-casting applications, as printed cores (parts) are immediately available for casting with no heat treatment required. 2) Phenolic binder, which is commonly utilized for printing sand moulds and cores, as it is best suited for high temperature pouring of castings. Very thin walls or thin pipes can easily be printed, due to the high heat strength of the core. Parts are easily cured using microwave technology. 3) Silicate-based binders, which are environmentally friendly as they burn off to form ethanol. These binders are increasingly being used for printing with low gas emissions during the casting process. Parts are easily cured using microwave technology. 4) Aqueous binders, which are typically encountered for bonding layers of powdered metal together. Once the parts are printed, they are placed into a furnace and the binder is burned out of the parts while powder particles fuse together in a sintering operation.

In binder jetting, it is not possible to use multiple feedstock powders owing to the nature of the technique. However, functional materials and compounds may be coated onto the feedstock powders and mixed with the bulk, meaning they would be distributed throughout the entire build. Another scenario is



Figure 6. An example of a multihead binder jetting system, where each printhead draws from a separate reservoir of binders.

directly incorporating them into the binders and delivering them through the printhead. If the functionality is to be located at specific locations of the part, then a separate printhead dedicated solely for depositing them may be used. However, it is crucial that the introduced materials do not negatively impact or prevent the binder from performing its adhesive function.

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Researchers have employed dyes and pigments to assist in understanding of the droplet deposition and layer formation in binder jetting. Lehmann et al.^[81] incorporated graphite nanoparticles (mean diameter: 50 nm) into the binder to create a better contrast for their investigations into droplet deposition and penetration. Similarly, Wagner et al.^[82] developed a binder jetting testing system to investigate fluid and particle dynamics occurring upon impact of jetted binder droplets onto a powder bed. In doing so, they added a small amount of fluorescent dye to the binder, enabling them to accurately monitor printed lines by illuminating them by UV light and subsequently performing image analysis on them for the purpose of analyzing the deposition quality.

As jetted parts are often porous, infiltration is a viable means for embedding functions, where the functional materials are incorporated after printing and before any sintering or postprocessing steps. Infiltration can occur by either coating or immersing the entire part into a solution containing the infiltrant of interest. Otherwise, functional particles could be suspended in an appropriate liquid carrier compatible with the inks or binders, and when the part is immersed these infiltrants can penetrate into the pores of the printed part. Additionally, the porous framework that results from the jetting could serve as a reactor for the nucleation and growth of "smart" materials. For example, appropriate chemical precursors, when sintered, are able to form a new material (such as a fluorescent quantum dot or a ceramic crystal).

A wide variety of applications are possible, including sensing, product identification and anticounterfeiting capacities, increased corrosion resistance, and potentially monitoring the quality of the build with optical markings, as will be elucidated further in Section 4.

3.6. Material Jetting

Material jetting (MJT) has several parallels to inkjet printing. A material "ink" is loaded into a printhead that deposits many fine droplets on the build plate. The ink is typically photocurable, and each pass of the printhead is accompanied by a pass of a light source that cures (solidifies) the ink, setting it in place and thus forming the laver. Once a laver is complete, the build plate is lowered by an amount equivalent to one-layer thickness, and the process is then repeated allowing the part to be built up in 3D. The inks are typically comprised of the target material accompanied by additives to make them more amenable to the jetting process, such as tailoring the electrostatic properties or viscosity. Inorganic inks can also be produced by creating colloidal suspensions of metal or ceramic nanoparticles. Both continuous jetting and drop-on-demand (DOD) deposition are possible, so is the possibility for producing fully inorganic parts. Systems typically have multiple print heads, thus allowing simultaneously printing of multiple materials, as shown in the schematic illustration in Figure 7.



Figure 7. An example of a multihead material jetting system. Each printhead draws from a separate reservoir of material inks, which are added dropwise to the build platform, after which they are photocured and subsequent layers deposited.

Of the techniques mentioned, material jetting is perhaps more amenable to the inclusion of functional materials during the build process, as custom inks can be formulated and deposited either discretely or ubiquitously via a separate printhead. However, care must be taken so that the functional materials are chemically compatible with the bulk "ink", and that they cure and bind in accordance with the bulk material.

3.7. Embedding Functionality in AM: Practical Considerations

Different AM techniques obviously entail different approaches to embedding functionality, depending on the materials in use and the specific processing conditions, which are summarized in Table 1 (data gathered from multiple sources).^[83–90] Some techniques are well suited to print multimaterial parts, like FFF. Other techniques take advantage of the numerous processing variables to locally engineer the part's microstructure and hence its functional properties, like EBM. In order to overcome the limitations of individual AM systems, functionality can also be increased by merging different AM technologies, or even additive and conventional manufacturing methods, in the same object.^[91] However, the most common avenue to imparting new functionality relies on adding a second material, which can be accomplished either by combining two materials of the same type (e.g., alloying two or more metals, or blending two or more polymers) or by incorporating a functional filler in the matrix in order to obtain a composite material. In both cases, the physical properties of the base material that govern its printability should not be altered, and this sensibly limits the range of appropriate functional agents. The options for embedding functionality are further narrowed down for those AM techniques that attain part's consolidation via thermally driven sintering or melting. Some thermally labile substances, like medicines, and cellular constructs can already be damaged by the temperatures required for sintering (SLS) or melting (FFF) thermoplastic polymers,^[92] whilst very few functional agents can survive SLM and EMB, whose processing temperature routinely exceeds 1400 °C for printing stainless steel and 1700 °C for printing titanium alloys, with local peaks in the melt pool above 3000 °C.^[88] In this



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 Table 1. Summary of AM techniques and key factors related to embedded functionality.

	PBF			DED	FFF	SLA	Binder jetting	Material jetting
	SLS	SLM	EBM					
Typical materials	Thermoplastic polymers	Metals, alloys	Metals, alloys	Metals, alloys	Thermoplastic polymers	Thermoset polymers (resins)	Metals, ceramics, polymers	Metals, ceramics, polymers
Processing temperature	60–190 °C (slightly below melting point for semicrystalline polymers)	Often exceeding t 1400 °C (above melting point of metal in use)	Often exceeding 1400 °C (above melting point of metal in use)	Often exceeding 1400 °C (above melting point of metal in use)	180–240 °C (slightly above melting point for semicrystalline polymers)	y Room temperature t	Room temperature	Room temperature
Environmental conditions	Inert atmosphere (nitrogen)	Inert atmosphere (argon; nitrogen)	High vacuum	Inert atmosphere for laser-DED vacuum for electror beam-DED	Air	Air (in bottom-up systems, the illuminated layer is naturally shielded from the atmosphere by the resin bath)	Air	Air
Ways of embedding functionality	Polymer blending	Alloying	Alloying	Alloying	Polymer blending	Grayscale printing	Functionalized binders	Multimaterial printing
	Polymer-matrix composites	In situ alloying	Metal–matrix composites	Metal-matrix composites (including FGMs)	Polymer–matrix composites	Thermoset–matrix composites	Postprinting infiltration	Additives
		Metal–matrix composites	Texturing	Multimaterial printing	Local enrichment	Fully inorganic parts	In situ nucleation and growth	Inorganic inks
		Multimaterial printing (limited)			Fully inorganic parts Multimaterial printing	s Multimaterial printing (limited)		Fully inorganic parts

regard, binder jetting is likely the most versatile AM technique for embedding functionality, as it works at room temperature and enables the incorporation of a broad range of functional fillers upon printing and postprinting, as clarified in the following sections through novel and original examples.

4. Opportunities: A Binder Jetting Case Study

To highlight some of the many opportunities for endowing AM parts with enhanced strength and new functional features, we present several concepts for embedding function into binder jetting as a case study. With the following sections, we aim to provide several concepts and elaborate opportunities for embedding function into binder jetting, which can spur future research in the field. It may also be possible to translate these concepts into other AM techniques (and especially to material jetting that, like binder jetting, works at room temperature), though the material formulations would require being tailored for compatibility to the processes inherent to those AM techniques.

4.1. Enhancing Mechanical Strength and Embedding Function with Bridging Particles

A key issue in binder jetting is the mechanical strength of green parts. These parts are typically weak and there is potential for them to be damaged or to become fragmented, ultimately leading to catastrophic part failure. These poor mechanical properties arise from the lack of cohesive bonding between the feedstock powders and the binders. Binder jet printing systems utilize a two-part polymeric or resin binder system. One of the two components of the binder is typically a sulfonic acid mix, e.g., xylene and toluene sulfonic acids, and is precoated onto the powders (sand or a metal). The other component of the binder is a liquid deposited by the printhead, typically a furfuryl alcohol which incidentally may be toxic. During printing, a layer of the precoated powder is spread over the build plate, and the printhead subsequently deposits the liquid part of the binder in the designated areas for forming the desired pattern. Upon contact of the liquid with the coated powder, a chemical bond is formed thus solidifying the powder. The by-product of this reaction is water, and hence the printed part requires a couple of hours heating at 100 °C to dry off, thus driving the reaction to completion.

One of the main issues with this type of system is ensuring that enough coated particles come in contact with the liquid component of the binder deposited by the printhead, as this can have a significant impact on the strength and robustness of the part. If not, the final product can be quite porous. Normally, the green part consists of an interconnected network of pores and cavities. This is a unique feature of binder jet printed builds when compared to conventionally manufactured parts, and has both pros and cons.

To avoid excessive porosity, it maybe possible to create an interpenetrating bridge of particles within the porous green part to enhance the mechanical properties, as shown in **Figure 8**. Nanometer- to micrometer-sized particles having the same





Figure 8. Schematic representation of coated sand particle as used in binder jet systems, along with surface functionalized silica particles (top). The surface functionalized silica particles infiltrate the porous sand printed object, and bind with the coated sand, thus increasing densification as well as mechanical strength (bottom).

composition as the build material, for instance, silica spheres in the case of sand printing, may be coated with appropriate surface functional groups (e.g., silanes) to specifically attach themselves to the sulfonic acid-coated sand grains. A range of particles with tuned surface groups and with appropriate surface tension could be studied for their efficacy as bridging agents to penetrate the green part, thus forming mechanically rigid bridges and improving the part's mechanical strength, as well as lifetime.

Currently, the main use of the sand-based printing is for making complex moulds in prototype casting applications. However, most of these moulds tend to be one offs owing to the nature and mechanical properties of the sand-printed products. By improving the mechanical properties, the moulds could be made more robust and reusable, increasing their lifetime. Besides moulds for sand casting, improving the strength and mechanical properties also has the benefit of enabling custom sand-based products to be built, thus significantly widening the appeal of binder jetting and enabling a much broader range of parts and products to be developed. Shapes with higher degrees of complexity could also be produced with greater mechanical strength.

As binder jet systems are not limited to sand-based materials, metals, ceramics, or combinations of these may also be printed and the respective green parts strengthened using this approach. However, a challenge for metal and/or ceramic parts is that they require a postprinting sintering step. Care must be taken so that the chemistries associated with both the binder and bridging agent do not negatively impact the part's performance after sintering. Through applying the concept presented above, it may be possible to achieve denser and less porous binder jet-based fully inorganic components, thus increasing the technique's appeal more broadly, particularly given that it is amenable to producing much larger builds than other AM techniques. However, the successful sintering of larger parts is influenced by shrinkage and ultimately limited by the size of the sintering furnace.

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4.2. Functional Nano/Microinfiltrants

Parts built by binder jetting tend to be significantly more porous and are distributed with networks of interpenetrating pores when compared with counterpart products made with other AM techniques like FFF.^[51] Sintering the parts after the build process can consolidate the powders. Micro- and nanometer-sized particles, whose composition will depend on the intended application, can be impregnated into the part and embed themselves within the larger porous network (schematized in Figure 9). In doing so, the presence of the infiltrant results in increased densification and much stronger and rigid builds. This can be achieved either by postprinting infiltration or by direct incorporation into the jettable binder materials, in which case they get left behind in the part when the binder is burnt off during the sintering process. Otherwise, infiltrants for increased density may be introduced after sintering, and then receive a second sintering step.^[93] Candidate materials for impregnation to induce an embedded function include a host of nanoparticles. For example, nanosized TiN and TiC may be incorporated into the porous networks for improving surface wear and hardness properties, as well as densification in Ti or Ti-alloys. Upon sintering they have the potential to improve surface finish and reduce roughness.



Figure 9. Illustration of infiltrant participles penetrating into 3D printed parts' pores and imparting functionality, such improving mechanical strength, increasing wear resistance, improving antimicrobial effects or even osteointegration of bioimplants.



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Another opportunity and advantage for binder jetting exists in embedding catalysts. There exists a vast array of catalytic materials which could be impregnated postbuild into devices such as custom static mixers, impellers, and other reactors.

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There is also great potential in the biomedical space, where a significant challenge is the ability for cells and bones to correctly graft and attach themselves to the implant. There have been numerous studies on the incorporation of bioactive materials, including bioactive glasses, into laser-based AM builds for bone grafting.^[94] However, a significant challenge is ensuring the bioactive phases do not react with the bulk implant material nor crystallize after exposure to the laser. As binder jetting is carried out at low temperature, it may be far more amenable for producing polymer-based implants bioactivated by the presence of bioglass or calcium phosphates (if postprinting sintering at high temperature is required, this may still damage the bioactive filler, though). Continuing on the theme of biomedical applications, the incorporation of Ag and ZnO nanomaterials could aid antibacterial function, particularly for medical devices.^[95]

4.3. Encapsulated Nanocodes for Product Identification

Embedding a unique code into AM parts may serve many useful purposes, allowing 3D printed objects to be located along the supply chain, and to be identified like a fingerprint for certification and anticounterfeiting purposes.^[1] Methods for integrating the codification materials and 3D printing hardware should be synergistically considered to create such a fingerprint. A number of approaches could be taken to achieve this goal, such as embedding molecules whose functional groups can be probed via vibrational spectroscopy (i.e., infrared or Raman) to yield a signature. Alternatively, luminescent particles may be used in clever combinations to provide a unique code. Luminescent nanoparticles, including quantum dots, are a class of materials that typically emit light in narrow bands (<30 nm full width half maximum, FWHM). They include, among others, metal-chalcogens,^[96] rare-earth oxides,^[97] and inorganic perovskites,^[98] each with unique optical emission bands. The combination of each uniquely

differentiable color, and its respective intensity, could be used in a similar way to lines on a bar or QR code. In other words, this unique combination may result in a "fingerprint". Using quantum dots presents a number of benefits. First, their fluorescence emission can be excited by a broad range of wavelengths, meaning different color-emitting quantum dots can be excited using the same light source. Second, given their narrow fluorescence emission bands, several different colored quantum dots can be blended with specific compositional ratios, or encapsulated within a larger particle, like a container, to provide a unique identifying code (described in Figure 10). Such container particles could be made of optically transparent polymers or SiO₂ systems, or others with similar optical properties, and could be manufactured in such a way that their size is submicrometer. This means the container particles (if properly formulated to be stable) can be incorporated into the binder of binder jetting systems and hence embedded into the 3D printed part without blocking the printhead. Interrogating the part with a light source of appropriate wavelength and dissecting the optical signature would hence reveal the unique identifying code.

The ability to produce encoded container particles of this small size and embed them within an AM component allows them to become a ubiquitous part of the component. Such container particles would be covert and small enough so as to not alter the look or impact the function of the part. Furthermore, given the high



Figure 10. Schematic representation of a "container particle," i.e., a macroparticle containing the color-coded nanoparticles, and its corresponding optical emission spectrum. The spectrum is comprised of the sum of the emissions from the constituent luminescent nanoparticles.



optical efficiency (quantum yield) of quantum dots, only a fraction of a wt% of container particles may be required, potentially limiting any adverse effects on the printed part's mechanical performance. Noteworthy, the ability to embed unique codes within a material during the manufacturing process as opposed to adding codes, identifiers, or tags postprocessing has the potential to provide time and cost savings, not to mention the advantage of producing a fingerprint that cannot be removed or tampered without irremediably damaging the part itself. Such technologies could allow component and product manufacturers, as well as other key parties in the supply chain, to track their items for quality assurance and for anticounterfeiting purposes.

4.4. Optical Tracers as Indictors of Build Success

Developing noninvasive methods for sensing part cracking or build failure is extremely challenging as the cause of the failure may arise from a number of processing or physicochemical variables, such as incomplete binding, degradation of chemical reagents, residual stresses, corrosion, etc. In binder jetting, build success is generally attributed to the ability of the printed part to maintain its structural integrity after printing, and it is important to know the part was built correctly, especially if there are costly and time-consuming post processing steps required. It may be possible to introduce tracers that can be probed optically to provide a rapid visual indication of where failures have occurred during the build. To achieve this, molecular dyes could be used whereby their optical emission is deactivated as a result of the chemical reaction between the two parts of the binder. In such a scenario, the dye molecule in the activate or colored state could be chemically anchored to the one part of the binder that is being jetted in the printhead. When the doped component of the binder is deposited over the powder bed, the chemical reaction with the second component of the binder on the particles' surface changes the electronic properties of the dye, thus deactivating its color. Careful inspection of the part for areas that are colored could reveal where the chemical bonds did not take place.

4.5. Optical Tracers as Wear Sensors

Another application for tracers is in the postbuild stages, such as for monitoring the performance of the part, particularly in high wear applications. It may be possible to provide a simple method for doing so by embedding optical layers in the build. Conceptualized in **Figure 11**, one or more layers of indicator materials, such as fluorescent ceramic rare earth oxides, can be embedded in specific regions of interest within a binder jet build. Upon cracking, wear, or corrosion, the exposed regions may be probed optically to identify where the optical signal is detected, providing a rapid indication of critical parameters, such as failure, cracking, and wear.

The same procedure can also be applied on as-built parts to spot out process-induced defects. This provides the operator with a clear indication of where and when to take appropriate action, such as component replacement, build process modification, or even information about the phenomena that triggered the failure or damage event.



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Figure 11. Schematic representation of a printed part containing optical tracer particles in selected areas (top). After wear, cracking, damage, or corrosion, the optical tracer particles are exposed (middle), and, when triggered, provide an instant indication (bottom).

Photosensitive, fluorescent ceramic powders, such as those based on rare-earth oxides, are capable of withstanding the temperatures experienced during postprinting processes, including sintering for metal-based binder jet printing. Moreover, these materials can survive temperatures associated with many AM processes, giving them the unique capability for being directly used in many 3D printing applications, not just in binder jetting. Though challenging to print using SLM, DED, or EBM, such materials can be easily incorporated with polymer-based techniques such as FFF. As an additional advantage, they are widely available and relatively inexpensive when compared to custom designed nanomaterials.

4.6. Distributed Embedded Chemical Sensors

The grand challenge for the next generation of sensors is to make them an integral part of components or systems, and not to be standalone devices. Embedded sensors can provide instantaneous feedback so that an appropriate action can be taken in response to changes in the component's local environment. It is desirable that such sensors can be distributed over a large area of the part and at the same time allow for sensing with extremely fine spatial resolution. Another key feature of such distributed embedded sensors is the ability to communicate their response to neighboring sensors, devices or user interfaces, to inform of changes that have been detected.

Binder jetting is highly amenable to distributing sensors throughout a part during the build process. Sensory nanoparticles can be incorporated into the binder and jetted through the printhead, either ubiquitously or at intended locations, if multihead printing is utilized. It may also be possible for the embedded nanoparticles to communicate with each other and relay information across the 3D printed part if appropriate chemistries are utilized. For example, quantum dots (including CdSe, perovskite, graphene, etc.) are able to absorb broad band light

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through an AM part. A) The 3D printed part receives external stimulus (e.g., a physical impact, local change in temperature or chemical response to eternal stimuli, etc.) in B) a localized region, causing the region to emit a signal (e.g., optical) to C) adjacent nodes which proceed to propagate the signal to D-F) adjacent nodes.

and yet emit light in very narrow bands. They can also be sensitized by either functionalizing their surface or the binder they are embedded in, to make them respond to different parameters such as chemical species, temperature, or pressure. Their response typically yields a change in their optical emission properties, and their emitted light signal could serve as input for adjacent molecules or dots in the system, thus triggering a cascade of optical information that facilitates signal propagation to neighboring particles (schematized in Figure 12). This interdot communication can induce particles in their vicinity to take an action, whether it be continuing the propagation of this information, or undertaking their own chemical response to somehow negate the effects of this measured change in local environment. For example, this could be the release of an inhibitor molecule, a neutralizing agent, a biosensing response, etc. The optical signals could also be used to actuate changes in the part itself.

5. Summary and Outlook

Additive manufacturing technologies offer far more than just a means for crafting objects in three dimensions. With the evolution of 3D printing technologies and the field itself progressing at a fast rate, parts with ancillary functions and embedded features will soon be the new norm. As outlined herein, many potential ancillary functions are possible, such as providing temperature and chemical sensing, wear and pressure detection, mechanical and chemical actuation, antimicrobial resistance, as well as part identification and fingerprinting for provenance tracking applications.

A number of potential approaches and functions have been identified which can be deployed for delivering embedded functionality into AM components and processes, and in the shortterm parts with such functions and capabilities will indeed emerge from the literature into the marketplace. Beyond that, there is potential for more far-reaching consequences, such as the 3D printing of robotic parts incorporating mechanical, electronic, and chemical architectures, and even biological features that not only replicate complex tissues and structures, but which are capable of exhibiting physiological and haptic responses which can be interfaced with human tissue.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

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