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Additive manufacturing of multi-material structures

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ABSTRACT

Additive manufacturing (AM) or 3D printing has revolutionized the manufacturing world through its rapid and geometrically-intricate capabilities as well as economic benefits. Countless businesses in automotive, aerospace, medical, and even food industries have adopted this approach over the past decade. Though this revolution has sparked widespread innovation with single material usage, the manufacturing world is constantly evolving. 3D printers now have the capability to create multi-material systems with performance improvements in user-definable locations. This means throughout a single component, properties like hardness, corrosion resistance, and environmental adaptation can be defined in areas that require it the most. These new processes allow for exciting multifunctional parts to be built that were never possible through traditional, single material AM processes. AM of metals, ceramics, and polymers is currently being evaluated to combine multiple materials in one operation and has already produced never-before-produced parts. While multi-material AM is still in its infancy, researchers are shifting their mindset toward this unique approach showing that the technology is beginning to advance past a research and development stage into real-world applications. This review is intended to highlight the range of 3D printed polymer-based, metal-metal, and metal-ceramic applications while discussing advantages and challenges with additively manufactured multi-material structures.

1. Introduction

Additive Manufacturing (AM) or 3D printing encompasses three essential concepts for a revolutionary idea: universal, practical, and efficient. When you consider how "universal" 3D printing is and what areas it has already influenced, the impact is quite remarkable. As it may be quite the leap from metal, polymer, and ceramic materials, imagine being able to 3D print something that everyone on the planet has at one point desired: food. Having the ability to think of your food, upload it to a printer, and see it automatically print your meal directly in front of you is no longer a thought for the future. Pizzas, intricately-shaped chocolates, and even cakes have been printed using 3D printing with little to no material waste, demonstrating the practicality and efficiency of the process. With 3D printing being a fully customizable process, even a simple trip to the kitchen would be influenced by the ability to print unique, mouthwatering meals at any time (Table 1).

While this customization is appealing to food-based application, 3D printing has generated a large appeal throughout the STEM field for designing personalized parts. Nike completely changed the way customers think about shoe performance when it unveiled a 3D printed football cleat that optimized cleat traction while decreasing weight [1]. General Electric created its new CFM LEAP aircraft engine with additively manufactured fuel nozzles, which reduced the component to only one part that was 25-percent lighter than the entire 18-part system previously used [2]. Even the medical industry and its patients have largely benefitted from the technology with 3D printed implants being tailor-made to specific patients to reduce surgery and recovery times. Tailoring these implants to patients also allows for a better-fitting product, which can reduce cosmetic defects and increase overall implant performance [3].

With its obvious universal practicality and efficiency, it is challenging to predict how the process will advance in the coming years. Multi-material additive manufacturing (MM-AM) is taking that first step forward by surpassing single material products to multi-material components that hold innovative promise. With all the advantages of 3D printing (material and resource efficiency, part and production flexibility, reduced production lead time, increased performance, etc. [4]), these components can have multiple materials with complex geometries and added functionality [5].

Take an ordinary chocolate bar. 3D printing the bar on demand in the size you'd like is rather intriguing but imagine taking it a step further. With MM-AM, you could take the same bar and introduce caramel, nougat, and maybe even a peanut butter coating to create a personalized candy bar with different flavors across the candy. By personalizing a candy bar to your specific taste through MM-AM, you can see the direct appeal of adding multiple materials into the same

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Table 1
Acronyms.

Acronym	Meaning
AM	Additive manufacturing
CAD	Computer-aided design
CBAM	Composite-based additive manufacturing
DED	Directed energy deposition
DLD	Direct laser deposition
DLF	Directed light fabrication
DMD	Direct metal deposition
DMLF	Direct metal laser fusion
DMLM	Direct metal laser melting
EBAM	Electron beam additive manufacturing
EBF	Electron beam freeform fabrication
EBM	Electron beam melting
FDM	Fuse deposition modeling
FGM	Functionally gradient materials
FRPC	Fiber-reinforced polymer composites
HAM	Hybrid additive manufacturing
IJP	Inkjet printing
LC	Laser cladding
LENS	Laser engineering net shaping
LMD	Laser melting deposition
LMWD	Laser-based metal wire deposition
MM-AM	Multi-material additive manufacturing
MMC	Metal matrix composites
MJP	Multi jet fusion
SLA	Stereolithography
UAM	Ultrasonic additive manufacturing
WAAM	Wire and arc additive manufacturing

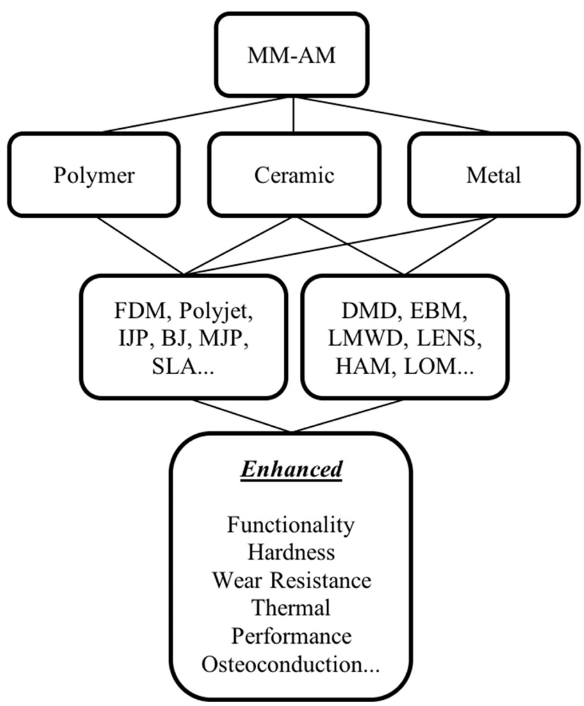

Fig. 1. Overview of some manufacturing and enhancement possibilities for MM-AM.

structure to get the most desirable combination. This same idea is being implemented into MM-AM of engineering materials, where instead of caramel in a chocolate bar to add sweetness, it could be a ceramic material in a metal bar to increase wear and corrosion resistance. The nougat could even be a harder metal to increase surface hardness, and the peanut butter coating could be a biocompatible coating for bone implant applications. This added functionality is the driving factor behind MM-AM processes, where region-specific functionalities can be placed in user-definable locations to create high-performance systems. A simplistic outline highlighting the general material combinations which make up these systems, what AM processes are most suitable based on material type, and possible material property improvements is presented in Fig. 1.

As shown in Fig. 2, traditional manufacturing processes must make system components separately and join them post-fabrication to create a composite part. The same goes with the chocolate bar analogy; the traditional bar has to go through multiple machines along the assembly line before the final product is made. With MM-AM, composite structures with graded or separate regions of differing materials can be built in one continuous step in a single machine, which enables composite parts to go directly from the design stage to the final part. Polymeric 3D printing was one of the first processes that advanced to MM-AM due to its simplicity and widely compatible material choice. Multi-colored components such as bike helmets, football helmets, and wearable gloves have been made with a very realistic appearance, shown in Fig. 3, as well as multi-functional smart polymer composites that change their geometry as a function of a changing environment, called 4D Printing. Although multi-material polymeric parts are exciting, they mostly serve as proof-of-concept prototypes that show the possibility of functional, multi-material systems.

To grow past this prototype stage and truly start to see a real-world application, 3D printing of metals has started to adapt to MM-AM of metallic composites. Single material 3D printing is what most industries are currently implementing into their products yet limiting the design to a single material holds back potential improvements that could increase the lifespan and performance of the part. Unique bonding styles of MM-AM processes can make a superior bond between multiple metals when compared to conventional processes because there are no weld seams to cause stress concentrations. And, with both materials starting in powdered form, multiple metals that are inherently difficult to combine via conventional methods can be more easily combined.

The unique ability of MM-AM, though, is that it cannot only combine two different materials at 100% composition but can create homogeneous areas of predesignated mixtures. This idea has led to combining multiple materials such as Inconel 718 and copper alloy GRCop-84, non-magnetic and magnetic stainless steels, and niobium on Ti6Al4V in various mixtures and are shown in Fig. 4. MM-AM processes have also shown that they can change metal properties by adding different phases, such as a secondary metallic phase, to new or pre-existing structures [23]. Furthermore, by controlling the amount of these phases the metal's properties can additionally be manipulated [24].

While combining multiple materials is influential, generating property-specific areas is likely the most significant ability of MM-AM as it can produce the part and its property variations in a single manufacturing operation instead of multiple steps. This advances metal MM-AM since homogenous mixtures can be made with metal-metal and metal-ceramic combinations at desired locations, just like in the chocolate bar analogy with chocolate and caramel combinations. Instead of being limited to conventionally welding two alloys together, functionally gradient materials (FGM) can be made by depositing metal or ceramic materials at a specific location to locally increase performance. When these material design choices are properly addressed, MM-AM can give more control over material properties when compared to conventional manufacturing processes to create these never-before-seen structures [25]. Metal-ceramic parts have been combined through AM processes to create metallic structures with high-performance coatings such as silicon carbide composite coatings onto Ti6Al4V [26]. Similarly, Vanadium Carbide (VC) was fabricated onto stainless steel for increased wear resistance (Fig. 5r–t), and an FGM consisting of Ti6Al4V transitioning to 100% alumina (Al_2O_3) was created to significantly increase hardness (Fig. 5o). Deposition of 100% alumina on an alumina substrate and graded alumina on stainless steel/titanium have also been demonstrated for multiple applications [29,30]. Reactive processes have been completed to create ceramic regions depending on the environment such as with *in situ* synthesized TiB-TiN-reinforced coatings

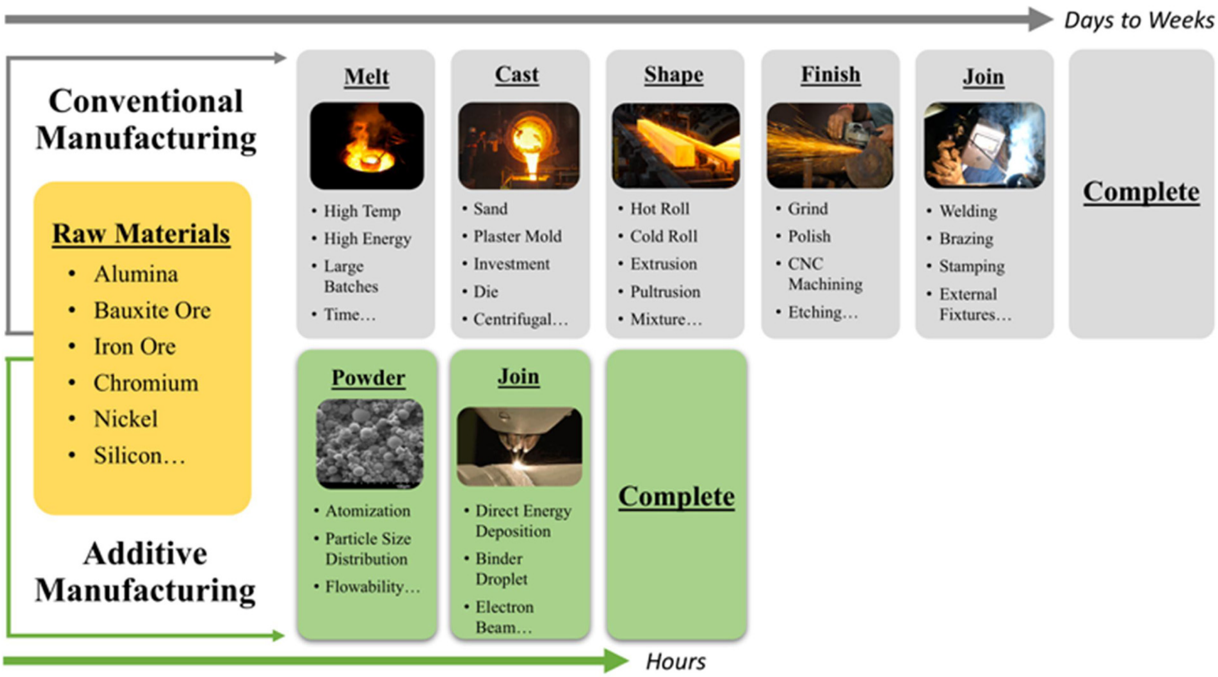

Fig. 2. Process comparison of conventional manufacturing processes versus AM for creating multi-layered structures. Images were borrowed from [6–12].

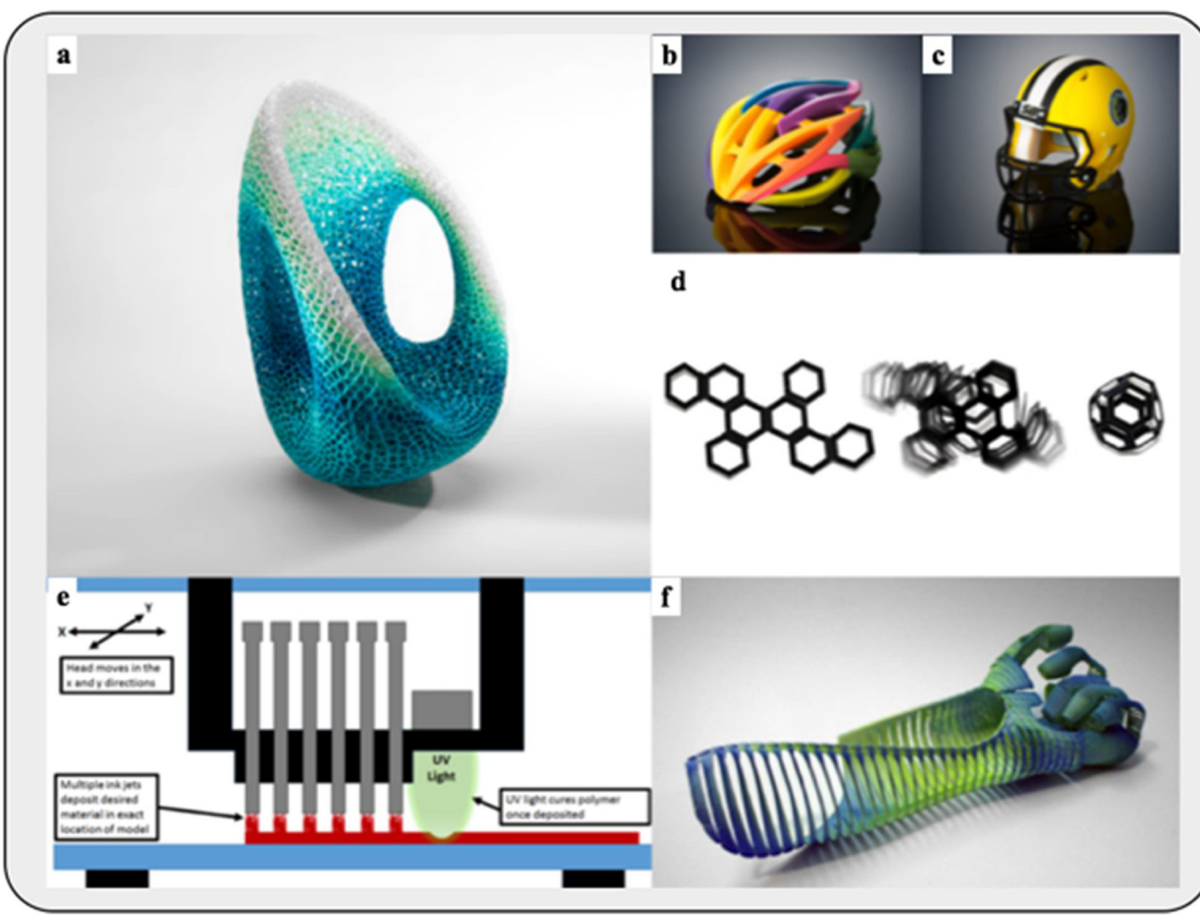

Fig. 3. Images of MM-AM polymer structures including (a) a "Durotaxis Chair" designed and printed by Synthesis Design + Architecture [13], (b) a realistic, multi-colored bike helmet and (c) football helmet 3D printed by Stratasys [14]. Also shown is (d) a self-assembling timeline of "4D Printed" polymers [15], (e) the Stratasys PolyJet system process [16], and (f) a 3D printed, multi-material motorcycle "glove" [17].

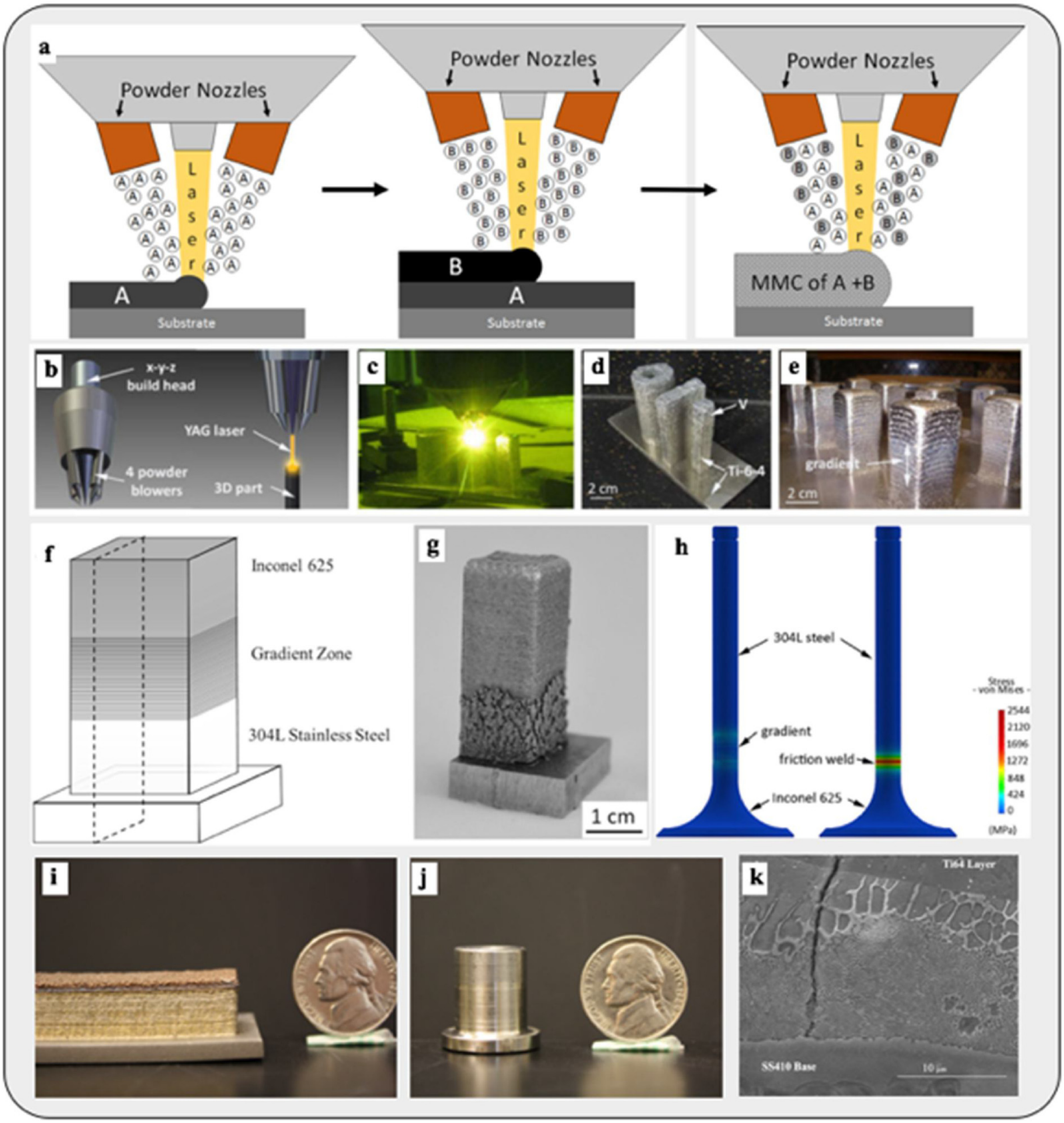

Fig. 4. (a–c) Schematic s of how powder based direct deposition can achieve gradient 3D metallic structures, as well as some innovative examples of metallic gradation. Examples include (d) Ti6Al4V to Vanadium, (f) stainless steel 304 L to Inconel 625, (i) Inconel 718 to copper alloy GRCop-84, (j) stainless steel 316 to stainless steel 430, and (k) some microstructures of a graded region from Ti6Al4V to stainless steel 410. Images borrowed from [18–21]. Fig. 4b–e were reprinted for free with no permission required under http://creativecommons.org/licenses/by-nc-nd/4.0/through article doi: 10.1038/srep05357.

on Ti6Al4V alloy [31].

MM-AM is advancing AM processes by making full assemblies, new materials, and precisely controlling material properties. The unique AM method of building layer-by-layer allows for the specific placement of material, and by doing so, the material properties can be controlled at exact locations, gradually added, and tailored for specific applications. MM-AM is a revolutionary approach that holds the power to influence and improve a wide variety of items we use in our everyday life.

2. Critical issues for MM-AM

MM-AM is based on combining multiple materials to improve the overall performance of one of the components. Whether it is multiple polymers, metals, or metal and ceramics, the combination of the materials has general limitations for the building process. The process itself can also have limitations toward real-world applications such as dimensional accuracy and size, need for post-processing, inability to process different material combinations at the same time under the same environment, etc. Some of these basic constraints should be discussed before going into material-specific processes and structures.

Simply put, the AM process starts by first designing a 3D component using computer-aided design (CAD) software, which can be used to make models, assign materials, and execute structural, thermal and other performance analyses. The 3D part is then converted into a sliced format that is used for the actual building process, which starts by fabricating the first layer onto a flat surface. Once this layer is completed, the manufacturing system moves to a point where the second layer can be built upon the first. This process is continued with

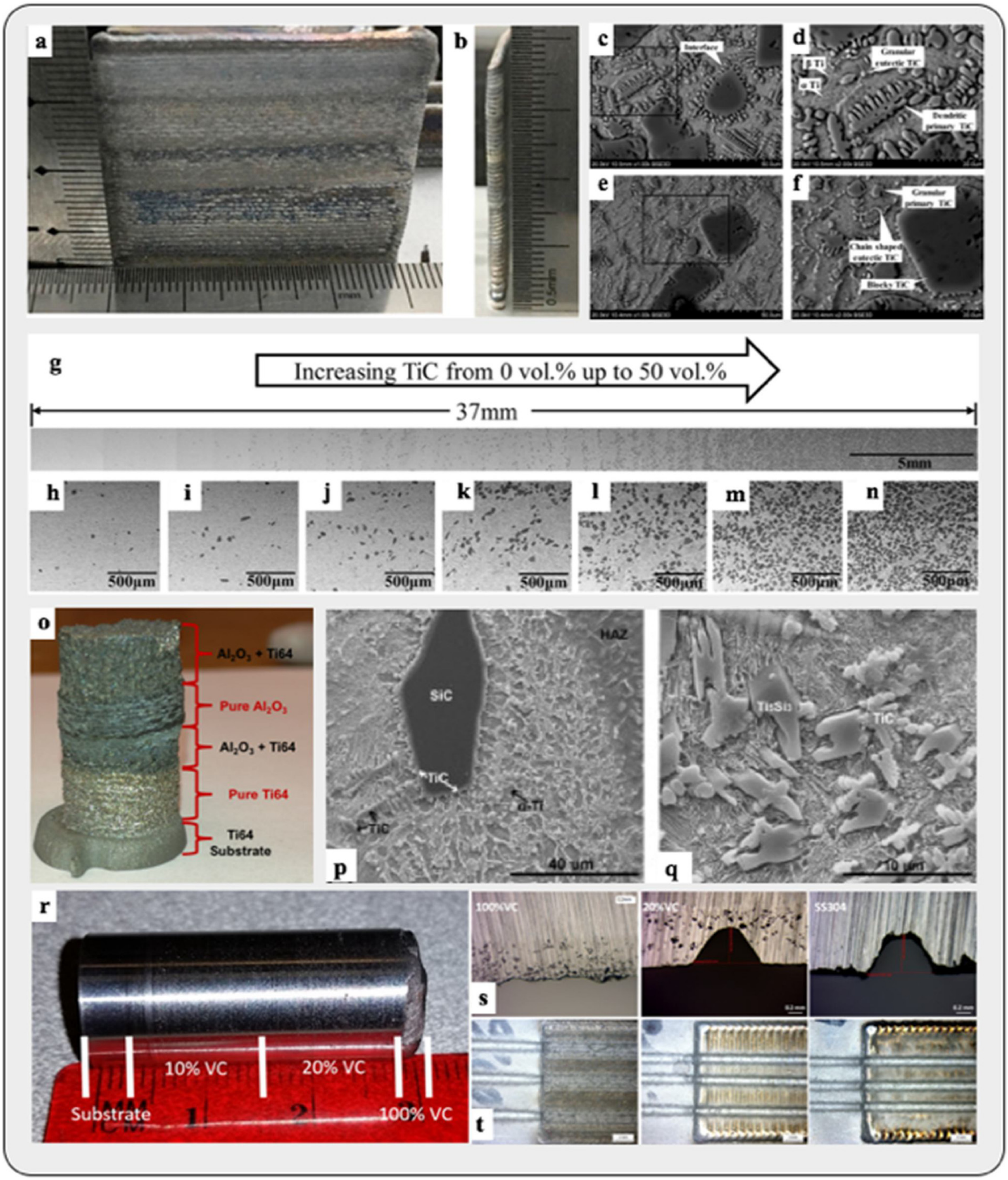

Fig. 5. Metal-ceramic structures and microstructures created through MM-AM processes. Unique structures include (a–f) TiC particle addition during wire feed processing and (g-n) particle morphology as a function of increasing particle addition, (o) novel Ti6Al4V + Al_2O_3 compositionally graded structure in the as-deposited state, (p,q) TiC reaction product in a SiC reinforced titanium coating, (r) cylinder of stainless steel 304 to VC gradation and its (s,t) abrasive resistance as a function of increasing carbide percentage. Images borrowed from [26–29].

changing layer geometries to fully and accurately create the designed 3D part, one layer at a time. With high-resolution capabilities, complex geometries in each layer can then be integrated into the final product. However, with differing materials, the joining process begins to show some limitations.

2.1. Joining processes for multi-materials

Current joining processes are relatively straightforward when combining similar materials, whether it is through conventional manufacturing or traditional AM methods. When combining dissimilar materials, though, many design factors need to be considered to create a strong, long-lasting bond. Aside from design factors such as material thicknesses and joint design, differences in thermal behaviors such as thermal expansion/contraction and mismatch in cooling rates during manufacturing and the real-life application play a large role in limiting the part's integrity [32].

A simple yet sometimes inefficient way to overcome these issues is

Table 2
MM-AM processes and some general advantages/disadvantages.

Processes	Advantages (A)/Disadvantages (D) (↑ High, ⥯ Moderate, ↓ Low)
Binder Jetting	A: ↑ Speed/resolution/material choice/functionality
MJP...	D: ↑ Stock powder amount
Material Jetting	A: ↑ Material choice/resolution
Polyjet, IJP...	D: ⥯ Speed/machine size
Material Extrusion	A: ↑ Part size, ↓ machine cost/energy input
FDM...	D: ⥯ Resolution/speed
Directed Energy Deposition-Wire Based	A: ↑↑ Speed, ⥯ material choice
EBF/EBM, LMWD, WAAM...	D: ↓ Resolution/support structure capability, ↑ material ductility required
Directed Energy Deposition-Powder Based	A: ↑ Functionality, ⥯ speed, ↑-⥯ resolution, integrated features
DLD, DMD, HAM, LMD, LENS...	D: ↑ Energy input and environmental/thermal control, ↓ support structure capability, post-processing usually required
Sheet Lamination	A: ↑ Part size/resolution, integrated features
CBAM, LOM, UAM...	D: ↑ Machine space/material ductility required

by bonding the two materials with an intermediate adhesive. Even though adhesive bonding of dissimilar polymers has proven to be a very effective process [33], two separately created components are still being joined. This means that if the end part requires the joining of two dissimilar components, a total of three manufacturing operations are necessary for the part's completion: manufacturing of part A, manufacturing of part B, and combining parts A and B. Three separate manufacturing operations can require excessive amounts of time and resources, especially if each of the operations require multiple stages to complete. While this “three operation” approach holds true for various processes such as combining similar and dissimilar metal plates or ceramic components, the unique ability of MM-AM to create, shape, and combine similar and dissimilar materials in one continuous process is an undeniable advantage in the global manufacturing arena.

With a wide selection of materials readily available, each with their own advantages and disadvantages, joining two distinctly different materials has been increasingly valuable to manufacturers. Joining two dissimilar materials does not necessarily mean the advantages of each material is desirable for the application; sometimes their disadvantages are exploited as well. One widely used example is manufacturing a transmission gear, which is in a highly abrasive environment. Instead of creating the entire gear out of a wear resistant material, such as a brittle ceramic that is inherently difficult to conventionally manufacture, the bulk of the gear could be made of an easily manufactured metal and the wear resistant ceramic could be applied as a composite coating in just the high-wear locations. This multifunctional variable can be added through MM-AM processes, creating gradient properties across a single component with limited post-processing.

2.2. Applications of MM-AM

To a large extent, conventional manufacturing limitations such as geometric constraints and small-scale production costs are a thing of the past when designing parts produced through AM. This is because AM has many advantages over conventional methods such as being able to have complex geometries, lower material cost, a near-complete user customization with no extra cost, material recyclability, and cost-effectiveness for complex small-batch items [4,34,35].

Though there is a lot of potential for AM and MM-AM, there are issues that need to be addressed [34,36,37]. Currently, only a few AM processes are used in modern manufacturing due to shortcomings such as surface finish, low production rates, quality control, repeatability, limited component size, and limited range of printable materials [35,36]. Additionally, the inability to predict and simulate the properties apart from the non-isotropic nature of the parts have limited the acceptance of these materials and processes by customers. It has also been expressed by companies that AM needs increased scale, bigger build envelopes, usable materials that are functional in high performance settings, and multi-functional smart responsive materials [38]. However, these problems are associated with AM as a whole. Due to MM-AM being even more extensive, it has additional barriers to overcome. These include CAD restrictions, material modeling software, designers not being familiar with the techniques, and material issues as stated previously [38]. All these matters need to be addressed before MM-AM can be largely introduced to modern manufacturing.

Though these drawbacks have limited AM's extensive use in modern manufacturing, the potential has continually kept research and development moving forward. More research grants are directed toward additive manufacturing research each year around the world. Some polymer AM machines have already adopted multi-material techniques [39]. MM-AM of metals and ceramics is inherently more challenging due to increased bonding difficulty between dissimilar materials and the amount of energy required to produce a multi-material system. Nevertheless, processes have been developed to incorporate multiple metals in one step as well as add metal matrix composites (MMC) and ceramic coatings to existing materials. Research will continue to solve these issues in congruence with new materials and processes being developed. Now that some general obstacles have been discussed, material-specific processes and innovative examples will be examined in the following sections.

3. MM-AM of polymers and composites

Before specific examples can be explored, it is important to note that out of the 7 generic AM categories set forth by ASTM International standards, 5 currently show the most feasibility for creating multi-material structures [40]. This includes binder jetting, material jetting, material extrusion, directed energy deposition (DED), and lamination-based processes, and some of their respective advantages and disadvantages are described in Table 2. Although the other two processes, powder bed fusion and Stereolithography (SLA), have shown some recent progress in MM-AM, the processes by themselves are fundamentally difficult to produce composite structures due to the mechanics behind adding a different material during fabrication.

3.1. MM-AM of polymers

Polymer 3D printers have always been on the forefront of innovation due to the simplicity and cost of dealing with polymers compared to metals and ceramics. Whether this involves simply changing the color or using two different polymers to build one part, systems have started to incorporate multiple material options to advance MM-AM.

Stratasys, which traditionally has been known for making fuse deposition modeling (FDM) machines, commercialized a multi-material 3D printer that can alter material properties and color using their PolyJet technology. It works just like a conventional ink jet printer, but instead of ink, it jets different polymers on a substrate in specified areas that are then cured by ultraviolet (UV) light (Fig. 3e), combining SLA and material jetting processes. Once one layer is completed, another layer of material is deposited and cured on top of the previously-deposited layer until a 3D part is done. This is unique as it can change materials during the build by mixing droplets of different polymers with varying properties, allowing the 3D part to have areas of varying rigidity, flexiblity, transparency, etc. [41]. Starting with 22 base resins, properties and colors can be specifically altered by blending various combinations of the resins, resulting in an astonishing 360,000 different material options [25]. Shown throughout Fig. 3, these parts demonstrate the color and material transitions capable of the MM-AM process for a user-definable, real-life appearance. With behaviors ranging from stiff to rubber-like, these base resins can be accurately mixed to create a hybrid part [25]. This can result in a part that has the characteristics of assembled components by changing properties in different areas. Not only can the material be changed to improve properties, but processing parameters can also be changed to achieve a similar effect. This material/process/property relationship is difficult to accurately determine but can be broadly related to the SLA process since it too imposes a layer-by-layer, UV-cured principle. De Solite SCR-300, a single acrylic-based photocurable resin, showed that under varying processing parameters such as scanning power ranging from 100 to 250 mW and layer thickness ranging from 150 to 300 μm, Young's modulus, strength, and toughness of the material increased with increasing power and decreasing layer thickness [42]. More specifically, the true stress-strain plot showed a fracture stress at ~13 MPa compared to ~5 MPa with the stronger sample having 150 μm layer thickness compared to the lower functioning sample with a 300 μm layer thickness [42]. With an increase in hatch spacing and curing depth, Somos 7110, an epoxy-based photopolymer, also showed an increase in Young's modulus from 2.40 to 2.60 GPa and ultimate tensile strength from 52.8 to 58.9 MPa while maintaining a constant Poisson ratio across all processing conditions in the green-state [43]. Improving properties of a single material solely through changing processing parameters now allows the 360,000 different material options to have a range of material properties, allowing an incredible amount of user-definability. This is the multi-functional and diverse capability of MM-AM that truly pushes the limitations of designers' imagination.

To further exploit the multi-functionality of MM-AM, Stratasys has also collaborated with MIT to make programmable materials that are adaptive to their environment. It is called "4D printing," where the fourth dimension i.e., time, allows the multi-material printed structure to change depending on the surrounding environment. This means the printed models are no longer constricted to a static shape but can be programmed to adapt to a changing environment, as shown in Fig. 3d. Using water as the activation energy to swell certain regions, a 2D composite structure comprised of accurately-placed rigid and soft polymers can transform into a 3D structure by controlling the swelling direction of the polymers through geometric design. The core of the technology is the machine, materials, and geometric program. A hydrophilic polymer was made that expands 150% when exposed to water. When the printer deposits the rigid polymer with the hydrophilic one in different configurations, it enables the polymer to fold in a predictable fashion when exposed to water. To do this advanced material placement, new software had to be made. In collaboration with Autodesk Research, a program was developed that allows for simulation of self-assembly and programmable materials, which in turn allows for optimization of design. It is believed that such technology could be used to create assemblies useful in applications varying from medical to structural [38].

3.2. Fiber-reinforced polymer composites

Unlike a composite made solely of polymers, fiber-reinforced polymer composites (FRPC) are of significant interest due to their light weight and high strength. AM is now being looked at to fabricate FRPC using conventional polymer AM processes [44]. Fiber-reinforced composite materials consist of small fibers that are aligned and dispersed in a polymer matrix. They are typically made of laminates laid on top of each other in different directions, which has proven to be an effective way to make strong, lightweight parts through conventional composite lay-up techniques.

The company Impossible Objects created a similar system that additively manufactured carbon fiber composite structures ranging from screws to airfoils through a process termed as composite based additive manufacturing (CBAM). These structures show the complex capabilities this process offers compared to conventional composite lay-up techniques that limit intricate design [45]. A 3D printer was also developed that incorporates inkjet-based 3D printing of polymers via curing by UV radiation along with the deposition of nanofiber mats. As the inkjet deposits a layer of UV-curable ink, it is subsequently cured using UV radiation, reheated, and then fibers are laid on the polymer mat. The fibers are cut to the mat shape and stamped into the mat, and the process continues layer-by-layer until the part is complete. Different fibers can be used for each layer, and the properties of the final part can be designed by type of fiber and direction of placement [46].

Table 3
MM-AM composition examples and their respective properties.

Compositions	Process	Properties (↑ Increase, ⇂↾ Moderate, ↓ Decrease)	
Polymer-based			
ABS + carbon fiber	FDM	↑↑ Tensile Strength, Modulus, ⇂↾ Porosity	[47]
ABS + Fe/Cu	FDM	↑ Thermal Conductivity, ↓ Tensile Strength	[48]
PCL + TCP	FDM	↑ Osteoconduction, Bioactivity, Non-Toxic	[49]
PLA + carbon fiber	FDM	↑ Flexural Strength, Modulus	[50]
Metal-Ceramic			
16NCD13 + TiC	LC	↑ Hardness, No Defects, Fine TiC Particles	[51]
AZ91D + Al + SiC	LC	↓ Wear, ↑ Hardness, Dendritic Microstructure	[52]
CpTi + Zr	LENS	↓ Wear, ↑ Cell Attachment, Hardness	[53]
SS316 + Al_2O_3	LENS	↑ Hardness, ↓↓ Porosity, Fine Grains	[31]
SS316 + BN	LENS	↑ Hardness, Wear Resistance	[54]
SS316 + YS-Zr	LENS	↑↑ Hardness, Micron-level Material Control	[55]
Ti6Al4V + TiC	LMD	↑ Hardness, Ultimate Tensile Strength	[28]
Metal-Metal			
CpTi + Ti-Ni-Si	LC	↑↑ Hardness, Wear Resistance	[56]
IN718 + Cu	LENS	↑ Thermal conductivity/diffusivity	[22]
IN718 + Ti6Al4V	LENS	↑ Functionality, Coherent Bimetallic Structure	
IN625 + SS304	DED	⇂↾ Hardness, Surface Finish, FGM	[18]
SS316 + SS430	LENS	↓ Porosity, ⇂↾ Magnetism Functionality	[69]
SS316 + Ti6Al4V + NiCr	LENS	Coherent Multi-Layers, NiTi and Cr_2Ti Phase	[19]
Ti6Al4V + Ti + Al	DMD	↑ Hardness, ⇂↾ Surface Finish, Cracks	[57]
Ti6Al4V + V	LMD	Coherent Bimetallic Structure, Crack-Free	[20]
Ti6Al4V + Nb	LMD	FGM, ↑ Thermal Performance Capabilities	[18]
Ti6Al4V + CoCrMo	LENS	↑ Hardness, Cell Proliferation, Wear Resistance	[58]

AM processing of FRPC is branching out from this mat-deposition technique to incorporate carbon fibers into polymer filament, which is slowly moving conventional polymer AM past a prototype stage for certain applications. One such application was the production of a 3D printed car by Oak Ridge National Laboratory, where a polymer composite was used to create the body of a 1965 Shelby Cobra in a feat that was never before seen. Other specific examples of polymer-based multi-material structures along with their respective property variations are outlined in Table 3.

4. MM-AM of metals and alloys

The design capabilities of AM coupled with the mechanical performance of metals and alloys create an unmatched connection between the designer and a high-performance final part. The most common AM processes for metals are direct metal laser melting/fusion (DMLM/DMLF), electron beam melting (EBM), laser engineering net shaping (LENS), direct laser/energy/metal deposition (DLD/DED/DMD), laser-based metal wire deposition (LMWD), and electron beam freeform fabrication (EBF) (or electron beam additive manufacturing (EBAM)). Hybrid additive manufacturing (HAM) processes are also being

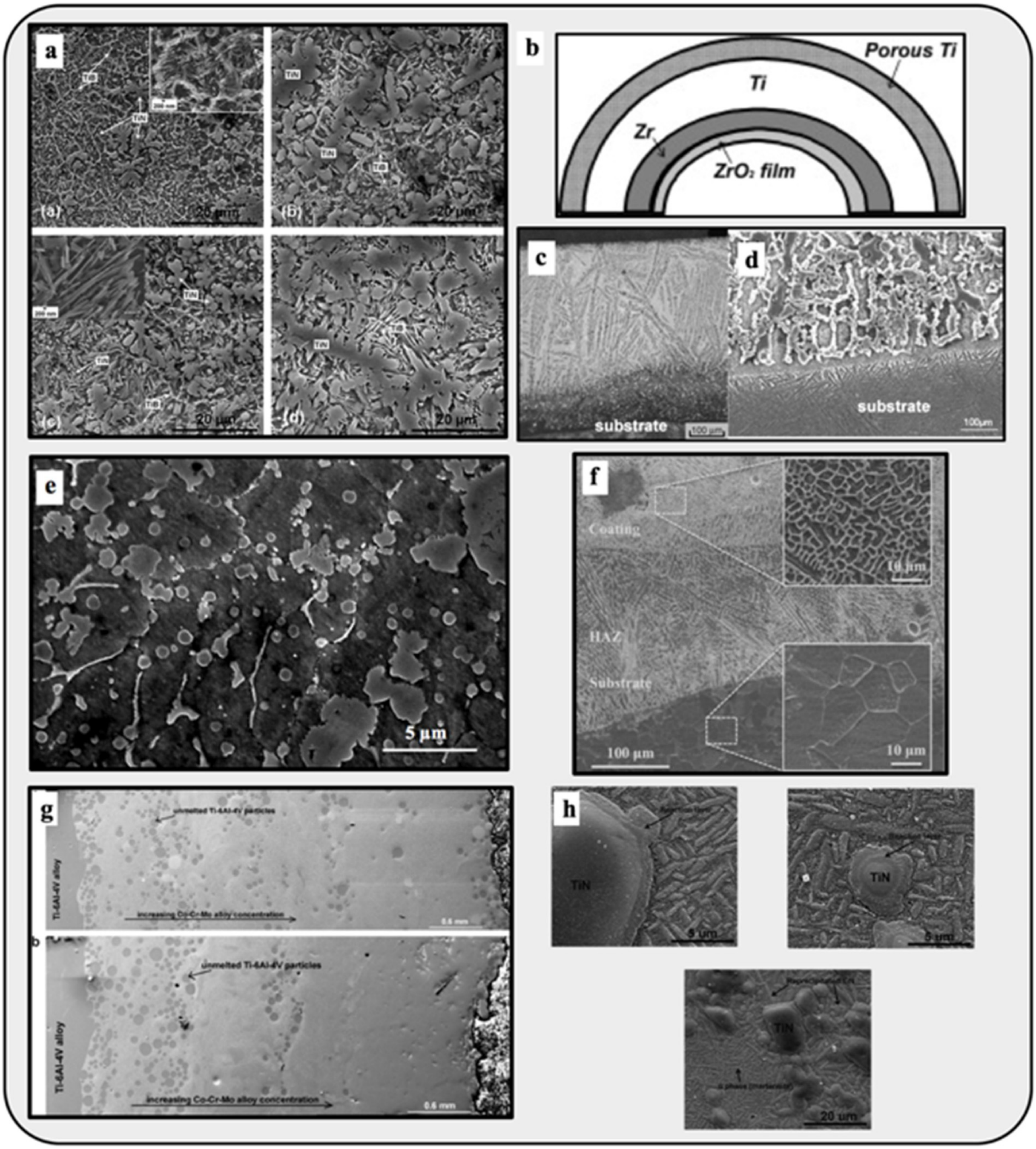

Fig. 6. Microstructure compilation of (a) nitrides in BN-reinforced Ti6Al4V [31], (b) MM-AM design [53], (c,d) intermetallic formation at the substrate-deposit interface of Ti_3Ni_2Si reinforced composite [56], (e) copper alloy on IN718, (f) substrate-deposit interface of SS316 + BN composite coating showing dendritic growth [54], (g) Ti6Al4V + increasing amount of CoCrMo [58], and (h) reaction layers around TiN formation in TiN-reinforced Ti6Al4V [59].

researched for metal AM to combine additive and subtractive processes. Through these common processes, high energy inputs from either laser or electron beam heat sources can provide enough thermal activation energy to form unique microstructures and phases, which are unachievable through equilibrium cooling. And, with sophisticated thermal management systems, gradient microstructures and phases can be tailored for specific applications. Fig. 6 highlights the unique microstructures and phases of some metal-based multi-material structures created through AM practices.

While there are many systems capable of additively manufacturing metals, most of these technologies are limited to single material AM due to various machine specific restrictions. For example, metal powder bed fusion processes, though reliable and widely accepted in both academia and industry, simply cannot easily accomplish multi-material processing due to the characteristics of the process and are therefore limited to single material usage. The incapability of processes like powder bed fusion to achieve multi-material processing will not be discussed here; instead, some processes capable of multi-material processing which hold the most promise for MM-AM as well as some innovative examples will be discussed below. Other specific examples of metallic multi-material structures along with their respective property variations are outlined in Table 3.

4.1. Wire fed direct deposition

EBF and LMWD are processes where a wire of desired material is fed

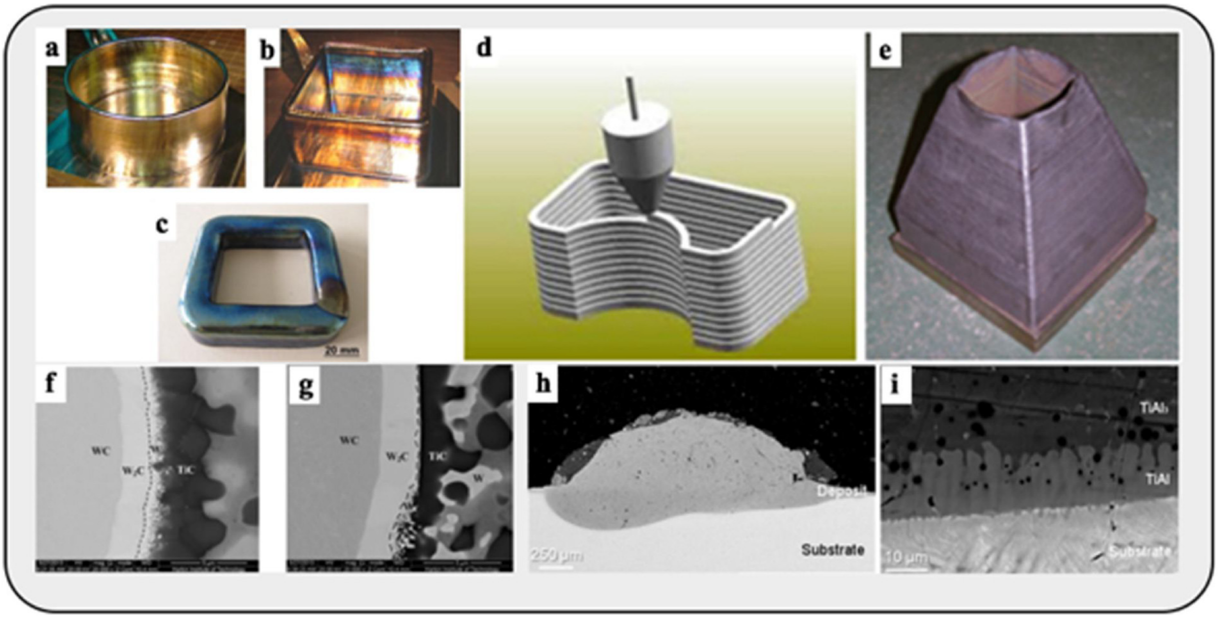

Fig. 7. Images of various wire fed direct deposition structures and composite microstructure. Images borrowed from [60–63]. Fig. 7h,i were reprinted for free with no permission required under http://creativecommons.org/licenses/by/4.0/through article https://doi.org/ https://doi.org/10.1016/j.jmatprotec.2016.08.031.

under an electron beam or laser that melts and solidifies the wire on the substrate along a design path. The part is then built in a layer-by-layer fashion until a complete component is made (examples of some large structures created by this process can be seen in Fig. 7). Though the fundamentals behind producing a final part are like well-established polymeric FDM processes, wire fed direct deposition is unique as the wire being fed under the beam can be easily changed during the process to make a multi-material part. Also, the only restrictions on part design are the number of wire feeders present and whether the material can be fed in wire form. To be in a wire form, the material must be ductile to withstand the forces necessary to reduce the material down to a thinned diameter. As this may be a limitation for advanced material structures, a large selection of raw materials ranging from titanium, Inconel, aluminum, nickel, nickel-copper, cobalt, tantalum, and even niobium as well as their respective alloys are readily available in a wire feedstock, to name a few [64].

From this selection, compositionally-graded parts can be built from a large variation of materials by combining different wires or even by combining wire with metallic powders from a separate feed during a single build [64,65]. Titanium alloy Ti6Al4V has been deposited as tubular and square cross sections at varying thicknesses to create large, smooth, single-material components (Fig. 7a–c) [60]. Other single-material bulk parts produced by direct wire feed as well as a schematic of the process are given in Fig. 7d & e. As another material is introduced into the system during fabrication, cross-sectional analysis and microstructural observations are necessary to understand its development during the successive layer-by-layer melting process. Fig. 7f–i provide some microstructures obtained in wire-fed composites, where Fig. 7f,g show microstructural changes with the continuous addition of tungsten carbide powder while depositing Ti6Al4V in wire-fed fashion. This combined wire feed/powder flow resulted in enforcement phases WC, W_2C, and TiC, which increased microhardness values from 320 $HV_{0.2}$ to 500 $HV_{0.2}$ in the composite layer [62]. Although the added powders are ceramic, multiple metallic powders can be added in the same sense to create metal-metal composites.

In addition to the mechanical advantages received from wire fed processes like increase in hardness, the technique has one noticeable processing advantage: deposition rate. The deposition rate of EBF processes has been reported up to 330 g/min, which is largely different when compared to the 10 and 12 g/min rate of directed light fabrication (DLF) and wire and arc additive manufacturing (WAAM), respectfully. However, with this fast deposition, high surface roughness and low dimensional accuracy becomes an issue [66]. To fabricate intricate metallic structures, a high dimensional accuracy and low surface roughness is required. Probably the simplest way to achieve this accuracy is by decreasing the size of material used for fabrication, as the laser used for processes like LMWD already has the capability for a small spot size which increases geometric capabilities i.e., dimensional accuracy. Reducing the material from wire form to powder form is the easiest way to achieve this as packing density increases and a scaled-down material generally equates to scaled-down resolution. Powder-based direct deposition techniques provide the best fit for the two requirements necessary to fabricate intricate metallic structures, with dimensional accuracy at approximately 25–130 μm and a surface roughness of 1–2 μm. It is partially because of this capability that powder-based direct deposition is making large strides toward innovation when compared to wire fed direct deposition [66].

4.2. Powder-based direct deposition

LENS, DLD, and DMD are direct deposition methods capable of multi-material fabrication, like wire feed, which use powdered metal instead of wire as the bulk processing material. These processes operate by flowing metallic powder under the focal point of a laser where it melts and solidifies on a substrate at a controllable rate. Shapes are then built by depositing material layer-by-layer with either the substrate or deposition head moving in a path suitable for each layer. This approach allows for MM-AM by dynamically changing which powder is deposited at specific times of the build. With multiple powder hoppers (the housing where bulk powder is stored in the machine during processing) applying multiple materials can be as easy as turning one hopper off and another on at the touch of a button. Fig. 4a–c shows how powder-based direct deposition processes generally work and how they can change material while manufacturing to create a layered structure of multiple materials. Not only can deposited powders be changed at any time during fabrication, but different powders can be pre-mixed and then deposited in a single stream. This makes gradient changes from one material to another possible, creating composite structures in user-definable locations where site-specific functionality is desirable.

The most important limitation of quality for these applications, however, is whether the deposited material will bond to the previously deposited ones. This in an inherent issue for most additive manufacturing processes and sometimes require material alterations, such as with polymeric AM requiring tackifiers in the thermoplastic to help bridge two successive layers. With complex interactions occurring during the melting and solidification stages with multiple materials, bonding issues arise from material-specific properties behaving differently as a response of thermodynamic evolution among the two materials. Mismatches in coefficients of thermal expansion, laser absorptivity, melting temperatures, and thermal conductivities are only some of the properties that sometimes inhibit multi-material combination. The metallic powder's ability to exhibit almost laminar-like fluid flow behavior (analogous to fine sand) instead of randomly breaking and cleaving (analogous to baking flour) also largely influences build quality for maintaining a constant and expected powder flow rate during deposition.

These limitations are currently being extensively researched to overcome bonding issues and build parts with strong material-material interfaces, and some of the alternative techniques are discussed later in this article. Companies have overcome some of these issues and have started to commercially develop multi-material parts using these processes [67]. DMG MORI, for example, has made a machine that combines direct laser deposition with 5-axis ultrasonic grinding. This machine can fabricate very intricate parts and has demonstrated making compatible multi-material parts by crafting a drill bit comprised of steel, Inconel, and tungsten carbide [68]. Another example is with LENS processes creating a stainless-steel tube that transitions directly from stainless steel 316L to 430L, effectively transitioning from non-magnetic to magnetic material. Compared to conventional welding processes, the LENS process created this continuous structure with absolutely no weld seam or large heat-affected zone with a smooth transition (Fig. 4j). Microstructures revealed a preferred grain growth direction at the interfaces of the deposited layers. Micro hardness values across the part's cross-section exhibited a smooth transition from the highest value of 266 ± 4 HV in the SS430 region to the lowest value at the SS316 substrate of 174 ± 3 HV. Magnetic functionality was observed on the SS430 side of the bimetallic structure [69]. AM through powder-based direct deposition has a strong ability to efficiently and accurately incorporate multiple materials into a single component, which is making this process increasingly exciting in the manufacturing field.

4.3. Hybrid additive manufacturing (HAM)

HAM is a manufacturing method which combines the cost-saving additive process with the dimensional accuracy of subtractive CNC machining. When a metallic part is additively manufactured by direct energy deposition, HAM allows for the part to be machined immediately after deposition occurs in the same system. This is largely different compared to the steps taken for conventional CNC techniques, where a block of a single material is placed into a CNC machine and is subjected to extensive subtractive processes to create a final part. A large amount of material waste is generated from the excess material during milling, which translates directly to manufacturing cost and environmental impact. With HAM, however, the initial block material is no longer present because the operator is building the part near net shape by direct deposition, requiring only surface finishing where necessary and creating little material waste. A schematic of this process can be viewed in Fig. 8. Also, because the additive portion is through direct energy deposition process, multi-material capabilities are present. With the subtractive power of CNC machining, surface roughness can be reduced before applying a second material for deposition to occur on a uniform surface, which is extremely important for fabricating dense, repeatable layers, especially for repair and coating purposes.

Furthermore, precisely controlling the surfaces of designed geometries are now available to the user directly after deposition. As shown in Fig. 8, systems such as DMG MORI's Lasertec 65 can additively deposit material via a 5-axis material deposition followed by precise 5-axis milling within the same system to create system-ready components [70]. The company Optomec also has this capability with its modular design that can integrate CNC milling, lathes, robotics, and more into one system, providing an incredible amount of motion control and precision during the manufacturing process [71].

A hybrid AM part created by Optomec can also be seen in Fig. 8, where CNC milling was controlled on various regions of the part while other intricate shapes stayed in the as-deposited state. This manufacturing evolution is largely different compared to conventional machining of an AM part where it is required to be sent to a separate CNC machine for final finishing processes. With HAM, multiple manufacturing methods are combined into one process to effortlessly go from additive to subtractive methods while maintaining a fixed part position [72].

HAM also works the other way; subtractive processes can occur before material is added, allowing for easy component repair. With the ability to take a worn part, place it into a HAM system, then prep and build onto the damaged area to restore it to its original state, HAM opens a wide range of material-saving opportunities in fields ranging from structural to automotive to aerospace and more. This allows for fabricating precise surface characteristics at regions in pre-existing and newly created structures while greatly reducing manufacturing cost and material waste [73].

Nevertheless, this process has its limitations to get from design to final part. Non-uniform cross-sections in designs causing CNC machining operations to become limited from overhanging structures, time required for tool changes, large pre-design considerations, and lack of coolants makes this process sometimes difficult for efficient production [72].

Once limitations are taken care of in future research, industries such as aerospace, automotive, medical, and defense that currently use metal AM would benefit from HAM due to its material waste reduction and shortened turnaround time [74]. Efficient part repair would also be appealing to these industries to limit large repair/replacement costs. With HAM's great potential to make AM processes even more efficient, future research is required to deal with the drawbacks of the process.

4.4. MM-AM of gradient metallic structures

The ability of DLD, DMD, and LENS to make gradient structures are advantageous for many reasons. For example, when bonding two dissimilar materials to each other, the chance of failure is generally higher at the interface because of the mismatch in properties as described earlier. As bonding issues are known to arise for large mismatches in material properties, the first step toward solving the issues is by reducing the magnitude of the mismatch. If there were a gradient change in material properties, the likelihood of material mismatch failures would be decreased [75].

A way to accomplish this without altering material compositions is by using a compositional layer as a sort of "bonding" layer between the two pure materials compared to a direct transition. Research has been done on designing methodologies for making FGM, which are materials with distinct material domains of graded composition. A new proposed methodology is discretization-based and moves away from a continuous material variation into a stepwise variation. A simple example of this can be material A directly transitioning to a composite zone of 50% A and 50% B, which then directly transitions to material B. A few examples of FGM in the as-deposited state as well as a schematic of the designed gradation can be seen in Fig. 4d–g.

Parts can be designed with gradient material properties and can be made by changing powder input. By doing this, the material behavior could be designed across the part by utilizing the changing material/mechanical properties of the material. In one example, a Ni-Cr part was

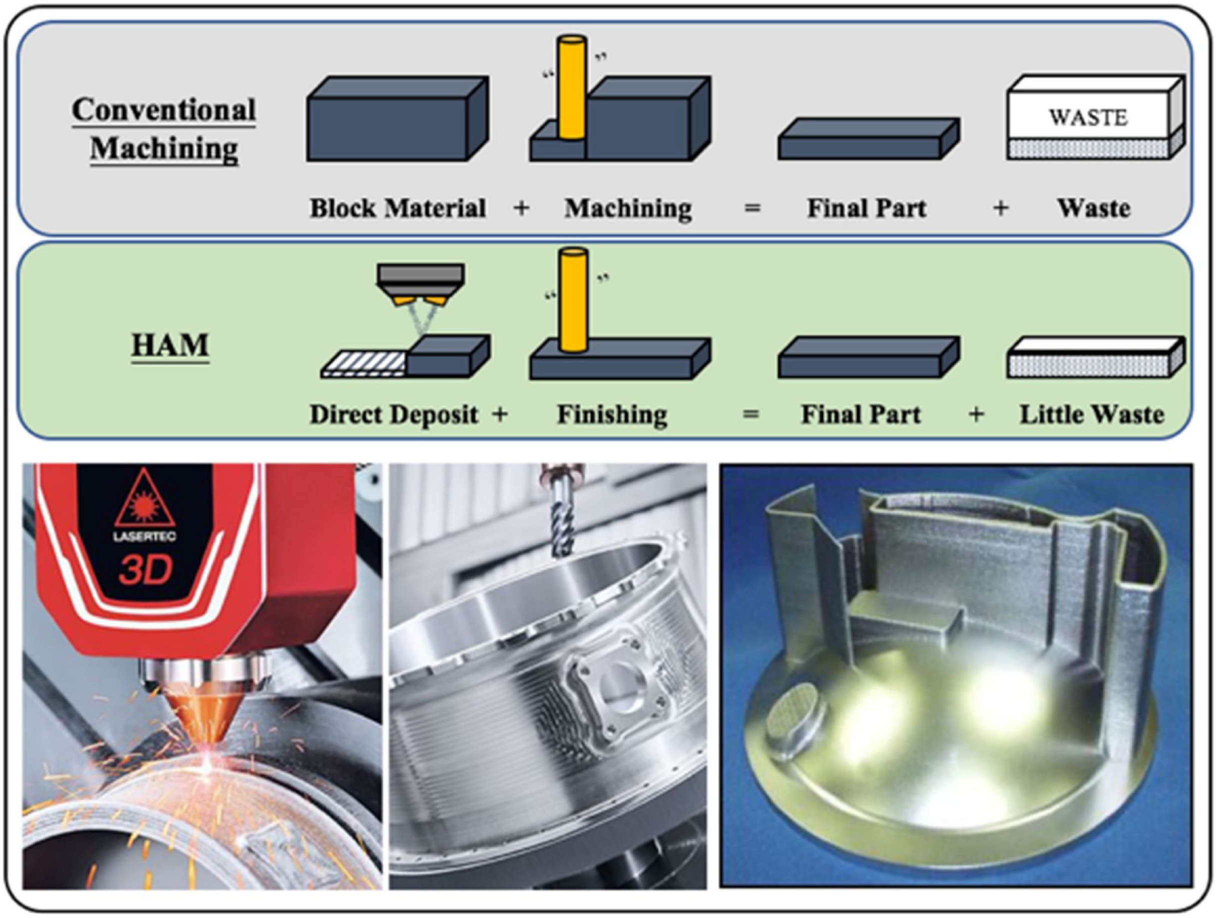

Fig. 8. A (top) schematic of how HAM contrasts with conventional machining to reduce material waste during manufacturing, as well as some real-life examples of HAM parts and system produced by DMG MORI (bottom left) [70] and Optomec (bottom right) [71].

made with a designed negative coefficient of thermal expansion (CTE) of dL/L = -0.00065 at 150° C. Ideally this process could be used to make structures that are piezoelectric, have a negative Poissons ratio, or make a ductile metal with a negative thermal expansion [24].

Compositional gradation also increases the overall properties and integrity of the part since weld-seam stress concentrations weakening joints are drastically reduced. In one case, finite elemental analysis has shown that a gradient transition from stainless steel 304L to Inconel 625 in an automobile valve stem has approximately 10 times less stress concentration at the transitioning zone compared to a friction stir-welded joint of the same materials at operating temperatures (Fig. 4h) [18]. Another FGM example is that of LENS-deposited Inconel transitioning to a copper alloy for increased thermal conductivity behaviors in high temperature aerospace applications (Fig. 4i). Once mismatching material properties can be taken care of through altering processing parameters, structures can be designed that are otherwise difficult to manufacture using conventional methods. The compositional gradation approach showed a gradual transition of Inconel 718 and GRCop-84 elements at the interface and columnar grain structures at the interfaces with Cr_2Nb precipitate accumulation along grain boundaries and the substrate-deposit interface. The average thermal diffusivity was measured at 11.33 mm^2/s for the temperature range of 50° C to 300° C; a 250% increase in diffusivity than pure Inconel 718 alloy at 3.20 mm^2/s. Conductivity of the bimetallic structures increased by almost 300% compared to Inconel 718 [22].

Additively manufactured porous structures, while seemingly unintuitive, can be classified as multi-material structures with a single material fabricated in such a designed way that air can act as the second material for internal and external porosities. These structures are considerably different to the dense MM-AM structures one usually imagines. This designed porosity has a dramatic effect on the performance of the material by intentionally weakening the structure and increasing surface roughness.

This idea was the foundation for engineering porous metal implants for biomedical application, as poor implant-tissue interactions and the high ratio of implant-to-bone strength in patients are the two major concerns for load-bearing implants [76]. Implant-tissue interactions are largely dependent on the surface roughness of the implant due to changes in surface energy and lack of surface area, which can cause issues in developing a strong interface between the implant and host tissue. Increasing surface roughness via external and interconnected porosity thus improves implant-tissue interactions by increasing surface area and allowing for mechanical interlocking to create a longer-lasting implant [76]. Using air as a second material for these biomedical devices also reduces the implant-to-bone strength ratio to more suitable levels. This is important for reducing a phenomenon known as stress shielding, which occurs when the implant is stronger than the surrounding bone and absorbs more load than the bone, eventually weakening the bone and creating an osteoporotic area in the surrounding bone [76]. With a worn bone surrounding the implant, the chance of the implant loosening is greatly increased and usually requires a revision surgery to reduce pain and replace the implant. Introducing air into the implant as a second material reduces the mismatch in strength while increasing the number of possible pathways for tissue to grow into the material [76].

Fabrication of porous cobalt-chromium-molybdenum (CoCrMo) hip stem implants through MM-AM has proven to reduce stress shielding while improving implant biocompatibility compared to purely dense

CoCrMo coatings [77]. With up to 18 vol.% designed porosity, these coatings showed a reduced modulus from 248 GPa in the conventionally processed alloy to 33–43 GPa, which greatly decreased the mismatch between natural bone with a modulus range of 3–20 GPa [77]. Similar coatings have also reported increases in surface hardness, wear resistance, and biocompatibility, potentially improving performance for articulating surfaces *in vivo*. A graded CoCrMo coating onto Ti6Al4V with 25%, 50%, 70%, and 86% CoCrMo on the top surface increased hardness to 947 ± 22 HV from 333 ± 16 HV in Ti6Al4V. Increase in CoCrMo introduced more precipitate formation with precipitates accumulated at the Ti6Al4V grain boundaries, and at 70% porosity precipitates that were once clustered along grain boundaries were replaced by a fine-grained two-phase CoCrMo-Ti6Al4V microstructure. These findings largely suggested that wear resistance of the graded structures would largely be improved compared to conventional Ti6Al4V implant material [58]. Gradient structures such as these influence a large amount of people in today's world by making longer-lasting, better-performing products to improve patients' way of life. FGM will continue to be heavily researched because of their advantages when making multi-material parts and their possibilities of altering and tailoring new material properties.

5. MM-AM of multifunctional metal-ceramic structures

Metal and ceramic AM is not a mature field [78]. Combining metals and ceramics into a single part is difficult due to the high mismatch in melting temperature and related thermal stresses. The temperature at which a ceramic can effectively melt and flow could be higher than that of a metal, which in some cases the temperature has caused the metal to evaporate before the ceramic could even begin to flow. This was observed while creating the Ti6Al4V-Al_2O_3 structure (Fig. 5o), where the Al_2O_3 powder absorbed enough laser energy before melting that the surrounding Ti6Al4V particles began to evaporate before the Al_2O_3 powder began to melt and bond. This is just one of the many issues when having to deal with bonding metal to ceramic during AM processes. Yet when the two materials are successfully combined, ultra-high-performance components and never-before-seen materials can be made. Some specific examples of these high-performance structures can be seen outlined in the text below and in Table 3.

One of the most researched fields of MM-AM deals with MMCs. MMCs have been an area of interest because they can be designed to have properties surpassing conventional alloys such as improved temperature, wear resistance, hardness, strength, conductivity, and weight [79]. The added phase or compound can strengthen the metal in a variety of ways, especially as a coating. First, the fast cooling of different constituents having different CTE result in cure stresses that can act as a barrier to crack propagation from compressive stresses, which is important for enhanced part life [80,81]. A second phase can also cause internal stress in the metal matrix because it causes a defect in the atomic order and structure. Both these phenomena result in internal strain which has been known to increase the hardness of the coating in laser cladding of CPM 9 V on H13 tool steel. Evidence of VC formation in martensite and retained austenite phase demonstrated a 300% hardness increase compared to the H13 substrate, and high energy inputs that led to localized expansion/contraction of materials developed approximately −1000 MPa residual compressive normal stress [81].

Fast solidification of metal around intermetallic reinforcements in MMCs also leads to strong matrix/particle bonding. This helps load transfer across interfaces of the phases and reduces the chance of cracking [82,83]. In the past, intermetallics have also shown to restrain dislocation movement on the grain boundaries according to the confinement theory. In the case of SLM $Al_{85}Nd_8Ni_5Co_2$ aluminum alloy, a composite intermetallic microstructure consisting of $AlNdNi_4$, Al_4CoNi_2, and $AlNd_3$ sub-micron phase was produced. These hard phases act as an obstacle that can deflect or arrest a crack and increase the effective mean path for deformation movement to allow for more deformation to occur before failure. Also, through the confinement theory at high temperatures, accelerated dislocation movement is confined to motion along grain boundaries that strengthens the material even further and results in a high compressive strength of 1.08 GPa at 300 °C for the aluminum alloy [82]. Many varieties of MMC have been made, including bonding hard ceramic elements such as WC, Mo-WC, TiC, SiC, VC, TiN, and NbC with conventional engineering alloys [24,51,52,56,57,79,81–107]. Fig. 5r–t gives an example of a compositionally graded stainless steel to VC cylinder with improved abrasive properties as a function of increasing VC percentage.

Some other specific examples of these MMC's include yttria-stabilized zirconia coating on stainless steel [55], compositionally and structurally-graded Ti-TiO_2 [108], and stainless steel to titanium bimetallic structures [19]. The high performance of AM yttria-stabilized zirconia coating was attributed to the obtained fine microstructural features that are unique to metal direct energy deposition techniques, specifically LENS. Rapid solidification produces fine microstructural features as well as columnar grains oriented along the coating thickness direction. These features are advantageous as the fine-grained microstructure had hardness values up to 2000HV and columnar grains have been shown to increase the life of certain thermal barrier coatings [106]. LENS was also used to process dense WC–12%Co composite coatings on stainless steel substrates [51]. The WC–12%Co coating hardness varied between 1171 and 1181 HV and an average dry sliding specific wear rate was in the range of $3 \times 10^{-6}\,mm^3/Nm$ and $6.5 \times 10^{-6}\,mm^3/Nm$ against Si_3N_4 articulating surface. Deformation and extrusion of cobalt phase followed by fracture and removal of carbide particles was found to be the predominant material removal mechanism [51].

LENS based DED process was also used to deposit a composite coating of SS304 and VC that exhibited higher hardness and wear resistance than the SS304 matrix. A compositionally gradient structure was made by deposition 100% VC on the surface. Laser processing yielded more homogenous grains of VC in the matrix. VC increased both hardness and wear resistance and further addition of a laser pass helped densify the ceramic filled layer. The 100%VC layer increased the hardness by 1450HV and lowered the wear rate by 95% compared to the SS304 matrix. Such high wear resistance was also reflected by the abrasive waterjet test where 100%VC was incredibly resistant to the harsh environments, showing no material loss compared to large material losses in 20%VC composite and the SS304 substrate [27].

Similarly, the addition of ceramic TiO_2 phase onto commercially-pure titanium increased surface hardness by four times by rapidly cooling the TiO_2 grains to a fine-grained structure and increased cell-material interactions during *in vitro* studies [108]. TiC particles have also been introduced as a reinforcement material during direct laser deposition techniques with Ti6Al4V, increasing hardness by nearly 94% through the presence of eutectic and primary TiC phase and the carbon in solid solution (Fig. 5a–n). Ultimate tensile strength of the composite was also increased up to 12.3% as a function of percent reinforcement phase addition, indicating that users can tailor the mechanical properties of the composite in desired areas [28]. TiN particles were also introduced in Ti6Al4V using LENS to increase hardness and wear resistance [85]. The average hardness of Ti6Al4V alloy increased from 394 ± 8 HV to 1138 ± 61 HV with 40 wt% TiN reinforcement. The coating reinforced with 40 wt% TiN exhibited the highest wear resistance of $3.74 \times 10^{-6}\,mm^3/Nm$, which is lower than the wear rate of laser processed CoCrMo alloy, $1.04 \times 10^{-5}\,mm^3/Nm$, tested under identical experimental conditions [85].

Various ceramic coatings have also been applied onto titanium to create metal-ceramic composites for biomedical application. The addition of calcium phosphate showed a significant increase in hardness and osteoblastic precursor cell line 1 (OPC1) cell proliferation during *in vitro* examination along with promoted biomineralization while a calcium phosphate addition decreased wear resistance by 92% compared to the original titanium base material [98,99]. It was found that an increase in laser power from 400 to 500 W and/or powder feed rate from 9 to 13 g/min increased the thickness of the coating but increasing laser scan speed decreased the coating thickness. Calcium phosphate addition changed the solidification grain structure from columnar titanium grains at the substrate side to an equiaxed titanium grains at the outside. When the scan speed was reduced from 15 mm/s to 10 mm/s, coating hardness increased from 882 ± 67 to 1049 ± 112 HV due to an increase in the volume fraction of calcium phosphate in the coating [98]. Calcium phosphate also developed a tribofilm during the wear study, which greatly reduced the coefficient of friction under wearing conditions and limited material loss [99]. Adding calcium phosphate (CaP) to commercially pure titanium (CP-Ti) and Ti6Al4V alloy via laser processing would decrease the material loss when subjected to wear was the main hypothesis. Such protection would arise due to the *in situ* CaP tribofilm formation because of the solid lubricant nature of CaP [99]. CaP tribofilm resulted in a decreased wear rate of 92% when 10 wt.% CaP was added to CP-Ti. However, 5 wt.% CaP to Ti64 decreased the wear rate by 70% [99]. Similar concept was also used in another work with CoCrMo and CaP, and parts were built using DED-based LENS system to enhance wear resistance in load-bearing articulating surface environment such as ball and acetabular cups for total hip prosthesis [91]. It was found that addition of CaP stabilized the ε (HCP) phase along with the more common γ (FCC) phase of the CoCrMo alloy. Discontinuous chromium carbide phase was also present. A tribofilm was found to develop on the surface during wear testing and led to the reduction in the leaching of Co and Cr ions. The wear rate of CoCrMo-3%CaP composite was one third as compared to that of CoCrMo-0%CaP composite. The tribofilm formation essentially transformed the CoCrMo-CaP system into an *in situ* self-protecting system [91].

These examples have generally followed the same processing ideology, where the reinforcement/coating material is deposited onto a substrate material in a single step to improve the overall performance of the substrate. This is in contrast to past efforts to create MMC, or even ceramic-ceramic composites, where some groups have utilized direct writing [109], freeform fabrication [110], robocasting [111], and FDM techniques [112] as a step toward fabrication of final parts intended to be removed from the substrate material. With most of these examples, part geometries are created with a ceramic slurry, which then require sintering and densification to create a final coherent part. Even though this is a multistep manufacturing process, complex structures of multiple ceramics or metal/ceramic composites can be created with active mixing. For example, direct writing of $BaTiO_3$, $BaZrO_3$, and $SrTiO_3$ ternary mixtures as well as Ni-$BaTiO_3$ multi-material structures have been fabricated. 15 different ratios of these oxide ceramics were created by only preparing one ink of each oxide combination and were dynamically mixed in the nozzle to change molar ratios. Sintered structures presented a homogeneous perovskite phase as confirmed through x-ray diffraction, and the mixing technology showed a great potential for mixing multiple materials in a predictable fashion [109].

Despite major improvements in performance, many of these extremely hard, metal-ceramic structures have certain manufacturing issues, primarily cracking, due to the large thermal shock associated with rapid solidification processes. Advancements still need to be made before multi-material metal and ceramic AM fully integrates into reproducible and reliable modern manufacturing. Progress and research on the topic has already started to increase the scientific community's understanding on metal-ceramic interactions, largely for MMC, during AM. Processes such as DLD and LENS have been studied to make MMC as a bulk alloy or as a coating. DLD easily makes MMC by adding a second metal or strengthening particle by mixing powders before deposition. Likewise, it can add these strengthening particles at any point in the build to tailor the part to the exact properties needed for the application. However, pre-combining powders is not the only method in obtaining a unique mixture of material and phase to obtain remarkable performance improvements. Reactive laser bonding processes also allow for new MMC that could not be created with conventional processes, which can create structures with impressive mechanical properties.

6. Reactive processes

Usually with any melting and solidification manufacturing process, environmental control is important for controlling any oxidation or other reaction with the environment to eliminate reaction products. Atmospheric control through shielding gas or operating in an inert atmosphere are widely used for current welding practices to reduce oxidation. MM-AM, however, uses this reaction to its advantage by having material react with the environment or another material present in the system. Reactive direct energy deposition AM processes take advantage of oxidation kinetics and reaction products of various materials during the build process, or *in situ*. As the system builds a part in the described layer-by-layer fashion, the energy input applied to melt the materials initiates a reaction between the two materials or the environment, thus creating a structure that contains each of the materials as well as reaction products [113]. Reaction with the environment coupled with rapid solidification processes retaining high temperature phases at room temperature can create varying phases that are difficult to create during conventional manufacturing. Phase types and concentrations can be controlled by changing the total energy input applied during manufacturing and by altering the composition of pre-fabricated powder. This process has been used primarily in DLD techniques because of the controllable environment during the reaction process and the ease of multi-material capabilities.

One DLD system in particular, LENS, has been used to create TiN reinforced and Zr-based coatings Ti6Al4V at varying TiN concentration [59,114]. When TiN reacted with the Ti6Al4V matrix, reaction layers occurred on the boundary of the particle and matrix and rapid cooling caused fine TiN precipitate formation mixed with needle-like alpha-martensite phase. Finer microstructures and an over 150% increase in hardness with the addition of 40% TiN in Ti6Al4V were observed [59]. An *in situ* Ti-Si-N surface coating has also been made by scanning a laser over the surface of a titanium plate in a nitrogen environment while depositing pure Si. As the laser melted the surface, the titanium and silicon bonded with the nitrogen in the environment to make a hard-ceramic phase. This coating had very high hardness and wear resistance compared to other Ti-Si-N coatings deposited using other processes [27]. Based on high hardness, coatings could be ranked as 90% Ti-10% Si-N coating (2093.67 ± 144 $HV_{0.2}$) > 100% Ti-N coating (1846 ± 68.5 $HV_{0.2}$) > 75% Ti-25% Si-N coating (1375.3 ± 61.4 $HV_{0.2}$). In the case of 75% Ti-25% Si-N coating, *in situ* formation Si_3N_4 phase was clearly evident from the phase analysis. Similarly, SiC-particle reinforced titanium has been created *in situ*, forming faceted titanium silicide Ti_5S_3 particles in alpha-titanium and Ti_5S_3/Ti phase and resulting in very high hardness and increased dry and wet wear resistance (Fig. 5p,q) [26]. *In situ* synthesized TiB-TiN reinforced coatings have also been created through LENS by first premixing Ti6Al4V and boron nitride (BN) before deposition. Once exposed to high thermal energies of the laser, the BN reacted with the Ti6Al4V to create TiB and TiN reinforcement phases which increased surface hardness by almost 5 times when compared to the original Ti6Al4V substrate [31]. This was accomplished by adding 15% BN to the mixture. Lowest wear rate of 1.90×10^{-6} mm^3/Nm was exhibited by Ti6Al4V-15BN composite coatings, which was even lower than commercial CoCrMo alloy used in the articulating surfaces of load-bearing implants.

Related findings have been reported in laser nitrided TiN-reinforced MMC on a NiTi substrate, where a dramatic increase in surface hardness from 250HV to a maximum of 900HV and two times wear resistance increase was observed. Dendritic TiN formed from constitutional supercooling gradually increased in concentration from the substrate interface to the surface, creating a compact layer of TiN and thus increasing topside surface. This microstructural evolution during *in situ* fabrication indicated that the laser-processed material improved the

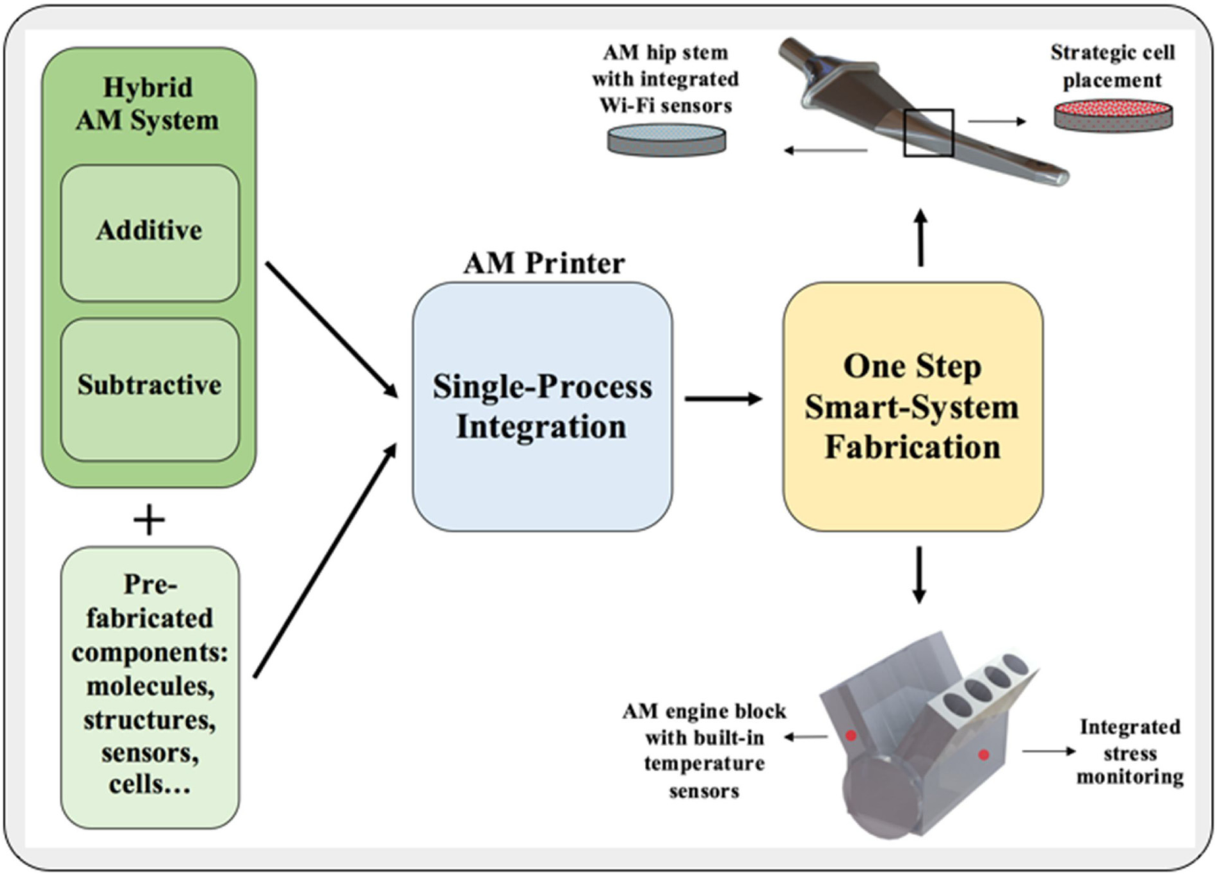

Fig. 9. Future of additive manufacturing, where hybrid additive manufacturing systems integrate pre-fabricated components to efficiently produce smart systems in one manufacturing step.

applicability of NiTi as an orthopedic implant as the increased wear resistance and hardness would increase the lifespan of the product [89].

Furthermore, reactive processes have led to a unique approach of creating Zr/ZrO_2 coatings on Ti for hip and knee implants. By running a Nd:YAG laser across a Zr coating, as well as introducing varying amounts of oxygen levels into the building environment, reactive processes occurred between the Zr and the oxygen and created a ZrO_2 phase that reduced wear rates by nearly two orders of magnitude as well as increased hardness to ~700HV when compared to the original Ti material hardness of ~200HV. The oxide film was composed of *t*-ZrO_2 and *m*-ZrO_2 phases. Higher amount of *t*-ZrO_2 decreased the friction coefficient and wear rate due to its high surface energy. As this study was done for biomedical applications, *in vitro* cell-culture experiments were also carried out to measure how well the system would interact in a biological environment, and it demonstrated that with the ZrO_2 phase present osteoblast cell adhesion was enhanced [53]. These reactive AM processes illustrate another perspective on how MM-AM processes can enhance the mechanical, structural, and overall performance of existing materials in one continuous manufacturing process for important applications.

7. Future trends and summary

As MM-AM encompasses increased functionality, it is safe to assume that future MM-AM techniques may not even require the printer to produce all the materials that are going into the system. HAM processes are already bringing a lot of attention to academic and industrial environments as its multi-material, multi-functional capabilities truly allow for fabrication and what usually is considered post production to occur in unison.

Similar to the analogy of the MM-AM candy bar, creating a single-material candy bar on demand through AM is currently feasible, and adding the caramel, nougat, and peanut butter coating is a vision that can be accomplished in the near future. While this is undeniably adding functionality, imagine the addition of a Wi-Fi-enabled temperature sensor in the heart of the candy bar that you could connect to and receive dynamic feedback. This feedback could provide signal to a Wi-Fi-enabled device, such as your phone, and alert you if your candy is getting too hot or cold and is beginning to spoil. Now, as impractical as having sensors in 3D printed food sounds, it serves as the analogy for the sensor-integrated candy as an immensely practical, smart MM-AM system that can provide feedback to the user in a certain environment. As shown in Fig. 9, HAM combined with pre-fabricated components in a 3D printer could produce dimensionally accurate smart-systems in one, continuous process. This could produce AM hip stem implants with sensors that constantly monitor implant-tissue interactions for infection and stress levels for real-time performance analysis. Similarly, integrated temperature sensors or strain gauges in AM engine blocks could produce a dynamic system that would constantly provide feedback on structural performance.

The list goes on for what could be integrated into a multi-material system, and it has already planted a seed in some minds as to how the limits of MM-AM could be pushed in the future. Automatically integrating pre-fabricated electronics into additive production and additively manufacturing the electronics themselves while printing a structure has already been proposed with the hope of sparking new ideas to overcome present-day technological challenges [115]. The future of the AM field not only relies on the technological strides being made daily but on the visions researchers and industries have who are exploring fundamentals and pushing the capabilities of AM.

Fortunately, today's rapidly evolving manufacturing and technology environments are fueling a new generation of bright engineers and designers. The industrial AM boom will only continue to expand toward a general audience as it has over the past decade. Just as it made at-home polymer 3D printers a commonality today, the world could eventually see a metal or ceramic 3D printer become common in an average household. To achieve this vision, though, future innovation in next generation structures using existing materials via MM-AM will surely need to revolve around cost reduction, improved performance, and advanced structural design.

Whether it is through advanced polymeric systems or unique direct energy deposition metal additive techniques like LENS, MM-AM will create a sharp, appealing contrast in the future of the manufacturing world. If the innovation of new exciting materials is not enough, revolutionizing the manufacturing procedure timeline could drive a large consumer base toward AM over conventional. AM systems have smaller environmental footprints than standard manufacturing plants. In a world with booming environmental and economic awareness, many businesses will likely transition portions of their production to AM. Single-operation production versus multiple-operation as well as on-demand, complex manufacturing has already started to shift many manufacturers' gaze from conventional techniques toward the advantage of reducing costs while improving design. With new designs for complex components, ranging from biomedical to structural to aerospace, innovative material fabrication from material synthesis is needed to push the limitations of the design to make components with improved performance. Product quality and reproducibility is also required for these components to truly be created on demand with full, reliable automation. As MM-AM systems gain more recognition for their ability to combine and produce new and improved materials, the technology will likely find its way into everyday products.

MM-AM can provide manufacturers with the capability to make components that were previously unheard of. It can allow for adaptable systems to be made as well as materials with superior properties compared to conventional production methods in one continuous manufacturing process. MM-AM machines bond materials to make composites, alter material properties, or make new materials completely. New machines will have the ability to make adaptable responsive systems that add a relationship between the user and the part never imagined before. As MM-AM advances in the world of polymers with "4D" shape changes, with metal matrix composites, and with metal-ceramic systems, the world will likely see emerging products that impact and improve items we use every day. MM-AM is an approach that will continue to develop throughout the near future and will cause a great deal of change in the way that designers, manufacturers, and even ordinary people at home will view products used in everyday life.

Declarations of interest

None.

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