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Review Article

A review of various materials for additive manufacturing: Recent trends and processing issues

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ABSTRACT

Tremendous growth has been witnessed in the field of additive manufacturing (AM) technology over the last few decades. It offers a plethora of applications and is already being utilized in almost every sphere of life. Owing to inherent differences between each AM technique, newer fields of research consistently emerge and demand attention. Also, the innovative applications of AM open up newer challenges and thus avenues for focused attention. One such avenue is AM materials. Raw material plays an important role in determining the properties of fabricated part. The type and form of raw material largely depend on the type of AM fabricators. There is a restriction on material compatibility with most of the established AM techniques. This review aims to provide an overview of various aspects of AM materials highlighting the progress made especially over the past two decades.

Abbreviations: CAD, Computer aided design; GM, Generative manufacturing; RM, Rapid manufacturing; RP, Rapid prototyping; DLP, digital light processing.

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Abbreviations

3DP	Three dimensional printing
AM	Additive manufacturing
BIS	Beam interface solidification
BPM	Ballistic particle manufacturing
DMD	Direct metal deposition
DMLS	Direct Metal Laser Sintering
EBM	Electron beam Melting
FDM	Fused Deposition Modelling
HIS	Holographic interference solidification
IJP	Inkjet printing
LENS	Laser engineered net shaping
LTP	Liquid thermal polymerization
LPD	Laser powder deposition
LOM	Laminated Object Manufacturing
SLS/SLM	Selective Laser Sintering/Melting
SLA	Stereolithography
SGC	Solid ground curing
SFP	Solid foil polymerization
SLC	Selective laser cladding
MJM	Multi-jet modelling

1. Introduction

Additive manufacturing (AM) is also known by various commercial names (including but not limited to) such as layered/generative/rapid/desktop/digital manufacturing, etc. AM was first commercialized around the 1980s and is still in the state of consistent evolution [1–4]. AM involves customized part fabrication in layers of virtually any intricacy and is accompanied by simultaneous reduction in process time owing to design cycle compaction, elimination of supply chain management, reduced scrap, negligible tooling requirement, reduction of manufacturing times, etc. [5–11]. Owing to the direct output-oriented nature of AM, remarkable reduction in energy or fuel requirement is obtained. This in turn lowers carbon footprints as well as greenhouse gases thus making AM score high as a green technology. Initial perception of AM as a strategy complementing traditional methods has now changed since its applications today surpasses those of the later [12–17].

AM refers to a class of techniques where objects can be fabricated directly from CAD design without tools or specially designed jigs/fixtures and involves minimal human intervention. Along with subtractive and formative techniques, AM forms a versatile aspect of modern world manufacturing. During the inception period, AM was usually referred to as three-dimensional printing (3D printing) which was actually a name given to process developed at the MIT lab. However, the press and industry became so fascinated with the term 3D printing that today it has become a term synonymous with AM and the MIT process later came to be called binder jetting. A variety of other names like generative/rapid manufacturing (GM/RM) are popularly synonymous with AM [18–20]. These techniques have undergone appreciable metamorphosis over the past few decades to emerge into their current form. The journey of their development has been noteworthy and the timeline has been presented by various researchers [21–26]. Advancements and corresponding applications which contribute to enhanced market diversity and technological compatibility of AM technologies are reported at regular intervals.

Remarkable variability and flexibility in attributes is obtained in the AM parts. Fabrication of some very unique parts for example, light hollow contours or mould cavities possessing internal cooling passages, etc. is the characteristic ability of the AM techniques. Appreciable economic advantages (exceeding 50% in general in aerospace/automotive sectors) can be achieved by replacing conventional manufacturing with AM techniques in many applications [2]. Design cycle is shortened by a huge extent owing to which products can be quickly brought to market. Metal parts with considerably high strength/weight ratios with no restraint on the shapes are obtained. Intricacy in geometry and feature quality is also ensured.

Apart from the above-mentioned strengths, AM techniques come under the class of green manufacturing methods since the scrap as well as noise pollution is greatly reduced in their usage. AM machines can be installed in an office environment which makes them worker friendly. Elimination of need for highly specialised workshops is also a favourable factor. Significant cost saving by elimination of jigs/fixtures that result from absence of tools is a characteristic feature of AM [27–29]. Simultaneous processing or nesting of parts by careful layout optimization adds another dimension of effectiveness to AM techniques [3]. The above stated factors suggest that AM is a candidate for tremendous savings in terms of time and cost while simultaneously enabling higher flexibility, quality and variability [7,30–36]. Designing and fabricating materials with tailored properties is quite easy by AM route and has been studied by various researchers [37–46].

An interesting point to note here is the fact that despite the tremendous progress achieved in the direction of AM techniques, a certain level of ambiguity is still observed. Also, there is an urgent need for research and review in several areas. One of the most important aspects is that of AM materials. Interesting research has been reported in the area of AM including AM material categories, smart materials and structures [12,47–49]. However, there is a requirement of a single platform that overviews the different material categories, single step and multi step AM processing techniques for different materials, advancements, challenges and so on in the field of AM materials.

This review aims to provide an overview of various aspects of AM materials highlighting the progress made in last two decades. It starts with a brief discussion on classification of AM techniques. Then, the types of AM materials including plastics, metals, ceramics, cermets, smart materials, etc. are discussed in detail by highlighting their suitability with different AM techniques. Various issues related to materials and their processing via the AM route are discussed in detail. This is followed by a description of the different binding mechanisms and challenges in the field of AM materials. Towards the conclusion, the paper is summarized with discussion on the future outlooks and summary. The focus of this

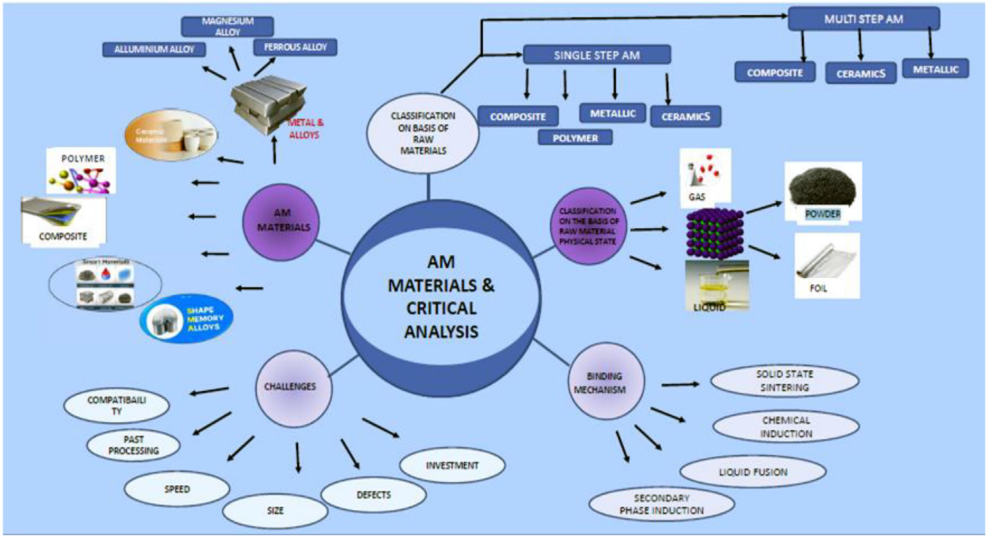


Fig. 1 – Material aspects covered in present review.

review is to analyze the different aspects related to AM materials as presented in Fig. 1.

2. Classification of additive manufacturing technologies

There are many AM processes commercially available today. Different researchers have classified AM techniques in different ways [3,6,50–52]. One of the common classifications is on the basis of ASTM-F42 committee guidelines according to which AM can be classified into seven categories. These categories are: vat photopolymerization (VP), material jetting (MJ), binder jetting (BJ), material extrusion (ME), sheet lamination (SL), powder bed fusion (PBF), and directed energy deposition (DED). The sequence of these categories is aligned as per their energy consumption. For example, least energy is required in case of vat photopolymerization (typically a laser of 40–50 mW) to cure the layers while high energy is consumed in DED (typically 4–6 KW). A brief discussion for all these seven categories is presented in subsequent subsections.

2.1. AM processes based on vat photopolymerization

VP is an AM process in which a liquid photopolymer in a vat is selectively cured by light-activated polymerization. In its general working, a light curable resin is collected in a tank and treated with either UV or visible light [53,54]. For a VP system, there are main two system configurations, viz. top down and bottom up [55]. In a top down approach, the position of the platform is just below the surface in the resin. The layer of resin above the surface is cured using light and then the platform is lowered down towards the bottom of the resin tank to allow new resin to flow in and next layer to cure. Fig. 2 (a) depicts a top down approach. In the bottom up approach, the bottom of the resin tank remains transparent and the light strikes from underneath the tank to cure the resin. The build platform then moves upward to allow fresh resin to fill in for the next layer. Bottom up approach is shown in Fig. 2(b). Similar to system configurations, there are mainly two types of exposure strategies viz, multiple scanning and flood exposure (as shown in Fig. 2 (a) and (b) respectively). The different system configurations as well as exposure strategies have their own pros and cons and should be chosen as per the suitability [56,57]. The VP category covers a number of different photo based AM methods which mainly include SLA, DLP, TPP and VAM.

VP techniques possess several benefits which mainly include: good surface finish, high speed, adequate accuracy, etc. [58–62]. These techniques also suffer from some drawbacks such as: need of post processing/curing, limitations on raw materials, need of support structures and so on [2]. VP utilizes polymer as well as plastic raw materials especially UV-curable photo polymeric resins.

2.2. AM processes based on powder bed fusion

In PBF, thermal energy selectively fuses regions of a powder bed [63]. Energy source may be in the form of laser, electron beam or indiscriminate electromagnetic energy [64]. PBF techniques utilize a high energy power heat source (thermal printing head) for selective melting and consolidation of build material (powdered form) to fabricate 3D components [43,65–67]. In its simplest working, a layer of build material of specified thickness is evenly spread over the build platform. The thickness of this layer generally varies from 30 to 150 μm [68]. Heat source fuses the desired area of deposited layer. Then, the build platform is lowered down followed by spreading of powder and fusion of next layer. Similar steps are repeated to develop 3D objects using PBF [69,70]. The PBF process is illustrated by Fig. 3.

Depending on the source of heat, PBF techniques are termed as laser beam based PBF (L-PBF) and electron beam based PBF (E-PBF) [72,73]. L-PBF mainly includes direct metal laser sintering, selective laser melting, selective laser sintering, etc. while E-PBF mainly includes electron beam melting [69,74].

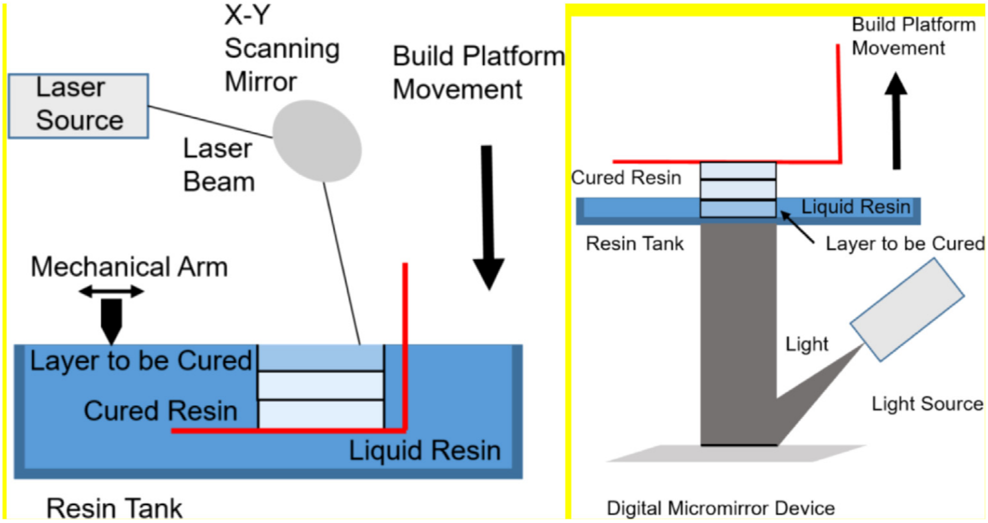


Fig. 2 – Schematic of VP: (a) Top down approach with multiple scanning; (b) Bottom up approach with flood exposure [55].

PBF techniques offer several benefits that mainly include: ability to develop highly intricate parts, large range of material options, nesting of parts especially in case of polymers and so on [75–77]. Material range that can be processed via PBF is quite wide. In addition to conventional materials, some special class of materials such as thermoplastics, polyamide, polystyrene, metals including Ti–6Al–4V, Inconel, steels, etc. can be successfully processed via PBF [78–86]. In addition to benefits, PBF techniques suffer from some drawbacks like support structures requirements especially for metals, need of post processing, high power requirements, high cost, large build time, etc. [2].

2.3. *AM processes based on material extrusion*

Material is selectively dispensed through a nozzle or orifice in extrusion-based AM processes which work on the fundamental principle of forcing pressurized semi-molten material through a nozzle either continuously or at varied rates for obtaining layers after solidification [87,88]. Control mechanisms for layer formation can either be temperature or chemical change-based [2,89]. The basic steps that are a characteristic of any extrusion-based technique includes: i) load material from chamber, ii) liquify by heat and/or pressure, iii) extrusion from nozzle, iv) layer deposition [90,91]. Schematic of extrusion based AM is presented as Fig. 4.

There can be different ways to classify extrusion based AM techniques. The most common way is on the basis of presence or absence of material melting. Common techniques which involve melting of material are: FDM, multiphase jet solidification, precision extrusion manufacturing/deposition, fused filament fabrication and fibre deposition [92,93]. Techniques that do not involve melting of materials mainly include: robocasting, bioplotting, direct-write assembly, pressure assisted micro syringe, low temperature deposition, and solvent based extrusion free forming [94–96].

Actuation of nozzles can also form one basis of classification for these processes. It can be achieved by different means

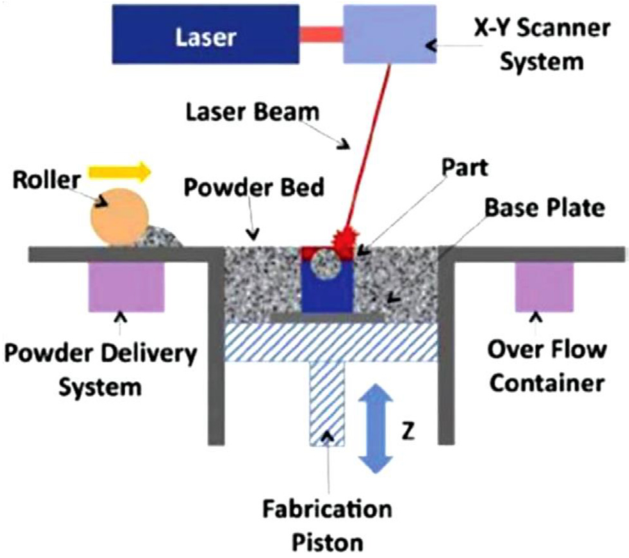


Fig. 3 – PBF process schematic [71].

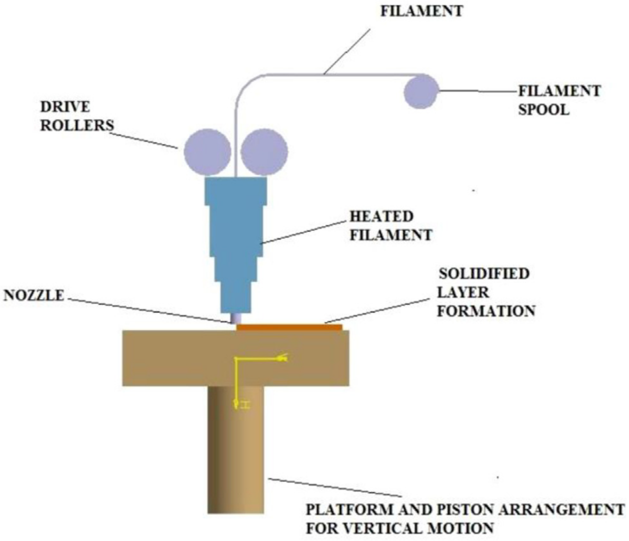


Fig. 4 – Schematic of FDM (material extrusion) process.

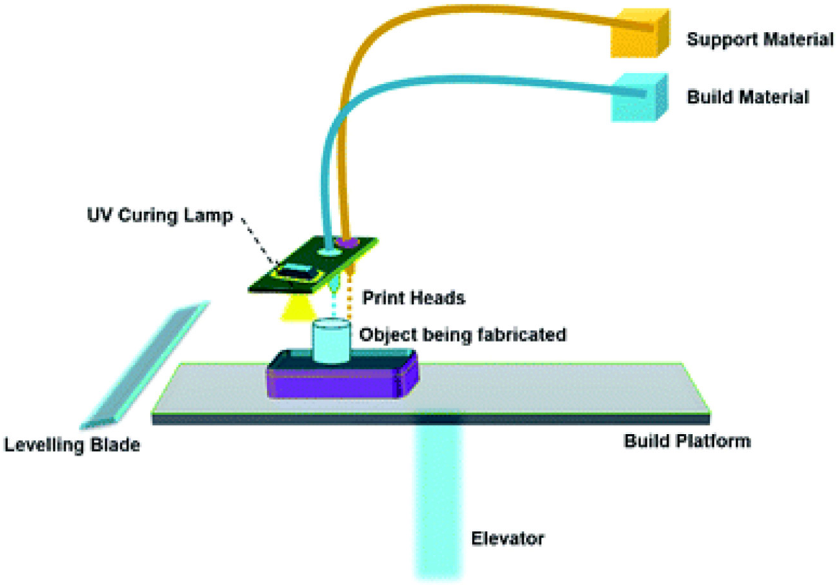


Fig. 5 – Schematic of MJ [111].

like pressure, solenoid, volume driven injection, piezoelectric, etc. [97,98]. Third basis of classification is the type of extruder used which can be plunger-, filament- or screw-based. FDM is most popular amongst these extrusion based AM processes and is used worldwide [99]. A variation of FDM is fused filament fabrication which finds extensive utilization in the concept modelling and prototyping applications and holds key to the immense popularity of these extrusion based AM processes [100]. Economical generation of parts for concept modelling, validation models, parts for indirect AM, special casting, etc. are popular applications of these techniques [90,101–107]. There are many challenges in the full scale utilization of these techniques which include: in-situ process monitoring, relatively inferior surface finish, standardization gaps, nozzle design and so on.

2.4. AM processes based on material jetting

MJ is an AM technique involving selective deposition of build material droplets [63]. MJ is synonymously termed as Polyjet (Stratasys) and Multijet (3D Systems) [108]. These techniques deposit droplets of liquid photopolymers from piezo/thermal printing heads which are cured using UV light lamps. In its simplest working, material (build) is injected over the build platform via printhead utilizing either piezoelectric or thermal means at pre-specified areas [109,110]. These deposited droplets get solidified and form the first layer. Same steps are repeated for depositing subsequent layers and developing 3D objects. After the layers are cooled, they are hardened and cured by UV light. Schematic of typical MJ technique is shown in Fig. 5.

MJ techniques offer numerous advantages such as ability of utilizing more than one printing head simultaneously, good surface finish, homogeneous material properties, etc. In addition to several benefits, these techniques suffer from some drawbacks such as need of support structure, limited raw material options, high material cost, limitation on size of printed object and so on [110,112].

2.5. AM processes based on binder jetting

BJ processes are those in which a liquid bonding agent is selectively deposited to join powder materials [63]. BJ is an AM technique in which selective deposition of liquid binder over a powdered build material takes place resulting in joining of powder particles. It is identical to 2D printing in principle.

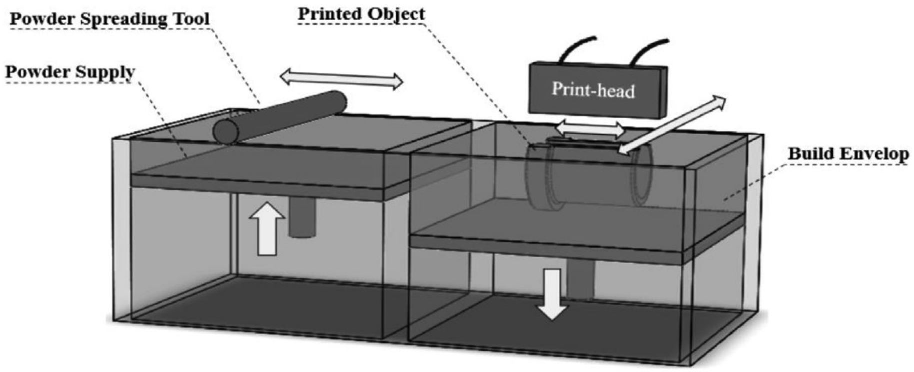


Fig. 6 – Schematic of binder jetting [116].

However, 3D objects are outputs of BJ as compared to 2D printing [113,114]. BJ offers relatively high build speed as compared to material jetting [115,116]. In its simplest working, build material generally in the form of powder is spread over the platform with the help of roller. Then, inkjet printhead deposits binder mostly in liquid state over the build material upon predefined areas to join the substrate particles and form a layer. Then, build platform is lowered to accommodate next layer and the steps are repeated till the complete 3D component is obtained. Schematic diagram of BJ process is depicted in Fig. 6.

BJ technique has several benefits out of which some are common with material jetting process. In addition, it has following distinct benefits: high speed, ability to develop coloured objects, high material compatibility, larger build volume, minimum or no residual stresses, etc. [117–124]. BJ has some drawbacks such as shrinkage, porosity defect, non-suitability for structural parts, etc. [125,126].

2.6. *AM processes based on sheet lamination*

Sheets of material are bonded to form a part in SL processes [63]. This technique utilizes thin sheets as feedstock materials to develop 3D objects [93]. These thin sheets are stacked, laminated and shaped to obtain desired form and size. SL techniques can be understood as hybrid AM techniques in which addition and subtraction of materials occur simultaneously to obtain the desired 3D component [127]. SL category has two main variants i.e. laminated object manufacturing (LOM) and ultrasonic consolidation (UC) [128]. Fig. 7 depicts schematic of typical SL technique. In its simplest operation, thin sheets are fed to the machine are initially stacked and cut using a suitable energy source (eg. laser beam). The cutting operation may be pre-stacking or after joining of sheets depending on the geometric requirements.

Lower raw material cost, no need of support structure, higher speeds, moderate machine set up cost, reduced thermal stress, lesser distorted/deformed parts, no chemical reaction, ease of fabricating bigger parts, etc. [130,131] are some distinct desirable aspects of sheet lamination process. A few limitations of this process include inferior bonds at interfaces, suitability only for sheet kind raw materials, inferior surface finish, less dimensionally accurate, inability to fabricate hollow components, non-reusable waste material, etc. [2].

2.7. *AM processes based upon directed energy deposition*

In DED, a focused thermal energy source is utilized to fuse materials by melting as these are being deposited. In its simplest working, DED techniques consist of three units namely a heat source such as laser, electron beam or plasma arc, feedstock unit and substrate bed having motion controls [132]. Fig. 8 depicts schematic of typical DED technique. Initially, a heat source is utilized to generate molten pool and addition/injection of filler material in the form of powder, wire or combination of both occurs [133]. This causes the feedstock materials to fuse and join to form layer-by-layer structures as the molten pool undergoes instantaneous solidification as soon as energy source is retracted from the deposition location [134].

DED techniques possess several benefits such as high deposition rates compared to PBF techniques, capacity to repair, ability to develop functional materials and so on [136–138]. In addition, DED techniques have some common drawbacks also that mainly include requirement of support structure, comparatively low surface finish, etc. [139,140].

Detailed comparison of these seven AM techniques based on various parameters is presented in Table 1.

3. Additive manufacturing materials

Materials have a vital part to play for complete understanding of AM processes [141–146]. A wide spectrum of raw materials is currently in use for different processes and appreciable quantum of research is under progress towards development of newer materials meant for specific applications. Polymeric materials, paper laminates and waxes are amongst the initial AM raw materials during the origin phase of AM. Plastics were another important group of materials used which still constitute important AM raw materials [147]. With due course and advancements, a variety of other materials like metals, composites, ceramics and so on have found utilization for various applications [146,148]. Consecutively, an impressive material spectrum is available these days for processing via AM route. Fig. 9 shows general classification of materials for AM.

As illustrated in Fig. 9 different kinds of materials including polymers, metals, ceramics, composites, smart materials, etc. are used as AM materials. Also, the state of their raw forms used as feed stock is different and discussed below.

3.1. *Raw material state for AM process*

The physical state of raw material used during the process is an important factor for understanding their appropriateness for any AM process. The compatibility of any form of feedstock which can either be liquid or powdered or wire or sheet for any AM process needs to be clearly understood. A group of AM techniques like stereolithography are based on curing of liquid resins [149]. Another group like laminated object manufacturing fabricates parts by joining sheet feedstock [150,151]. Yet other group melt powdered materials like selective laser sintering to obtain 3D parts [152]. A few AM techniques are based on melting of wired materials like the materials to develop the layers such as FDM [153]. Generally, material in liquid form results in better deposition which in turn implies that polymers and their derivatives offer convenience which can be accounted to lower processing or melting temperatures during process. Metals as well as ceramics possess high melting points when compared to polymers [154]. Processing ease is normally higher for polymers followed by metals and ceramics. In case of metals and ceramics bonding is appreciably difficult as compared to polymers owing the higher melting points of the prior two. It needs to be clearly understood that every AM process offers unique advantages as well as limitations and possesses compatibility with different physical forms of raw materials. Fig. 10 presents material type and state suitability for different AM techniques.

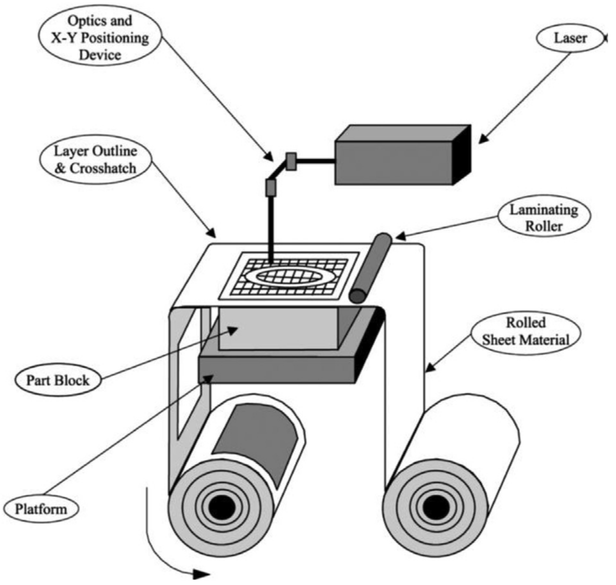


Fig. 7 – Schematic of LOM [129].

Classification of AM techniques based on state of raw materials is presented in Fig. 11.

A comparison of different type of raw materials (metal, polymer and ceramic) along with their state of fusion and processing strategies is presented in Table 2.

A detailed discussion on different types of materials and their corresponding issues is presented in the subsequent section.

3.2. AM of polymers

Polymers are widely used AM materials. Fabrication of plastics, polymeric graded materials, polymer matrix composites constitute some of the major areas where polymers are utilized in AM [157]. This can be attributed to lesser melting/curing temperatures, enhanced chemical stability as well as tendency to flow smoothly both in molten as well as softened states of the polymers. Processing of polymeric materials in AM can be in any physical state (liquid/powdered/sheets/wire) [158,159]. With careful selection of processing technique and compatible polymer, these can be processed by almost all fusion-based AM processes. However, three AM techniques that are commonly utilized include photopolymerization, material extrusion and material jetting [160–163]. Thermoplastic polymers as well as UV-curable polymers both constitute the most prominently utilized polymeric AM materials. In addition, FDM, SLS, inkjet printing, etc. have proven capability to develop polymeric components and polymer composites [164–166].

Polyamide, poly-lactic acid, nylon, acrylonitrilebutadienestyrene (ABS) and polycarbonate are commonly utilized thermoplastic polymers possessing AM process compatibility. All of these display the characteristic hardness at room temperatures. Fundamentally, extrusion based technique is based upon identical principle of melting by heating and subsequent solidification during deposition. PBF techniques utilize UV-curable polymers [167] where a monomer selectively polymerizes in presence of photo initiator in vat with the help of a light source. Apart from thermoplastics and UV-curable polymers, processing of elastomers (soft polymers) especially thermoset ones is also accomplished by AM route. It is however a difficult task and generally necessitates copolymer material systems i.e., combining elastomers with thermoplastics since these provide creep and hence facilitate ease of processing. Fig. 12 presents an overview of polymeric and monomeric materials used in AM.

3.3. AM of metals

AM offers flexibility to fabricate simple as well as intricate metallic parts of virtually any complexity. It has numerous advantages over traditional metal processing techniques. Past two and a half decades have witnessed tremendous growth in metal AM as compared to the limited work accomplished in this field during the initial years of advent of AM techniques [169–176]. Modern industrial world has reached a stage where

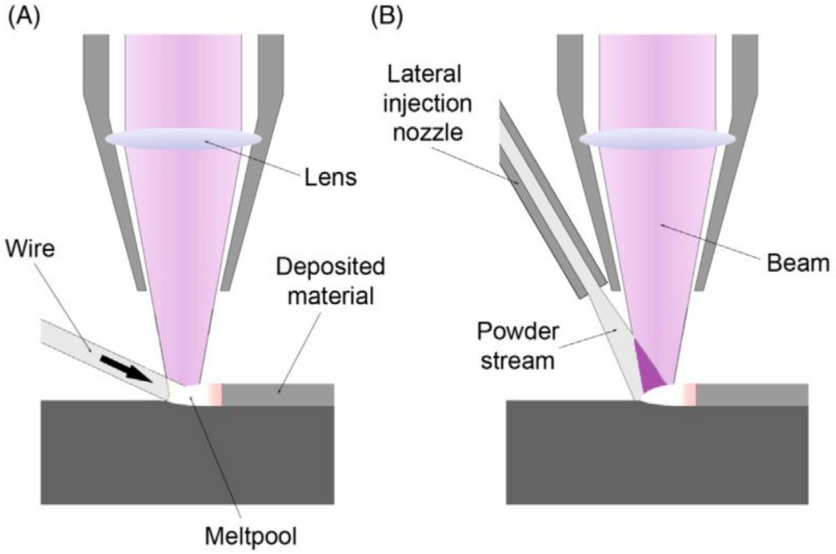
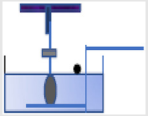
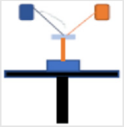
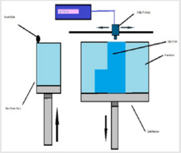
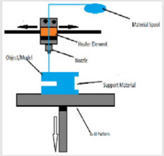
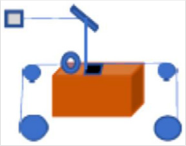
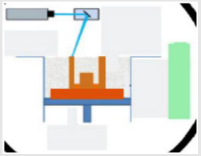


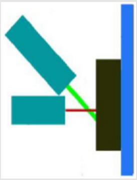
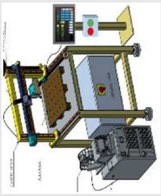
Fig. 8 – DED process schematic (a) wire based; (b) powder stream based DED [135].

Table 1 – Comparison of seven ASTM categories of AM: VP, MJ, BJ, ME, SL, PBF and DED along with their working principle, strengths, limitations and so on.

	Process and its line diagram		Commercial Models	Main Principle	Working Principle	Strength	Limitations	Typical Materials	Printing Resolution
Families of Additive Manufacturing	**Vat Photo-polymerization**		*SLA - Stereolithography Apparatus *DLP- Digital Light Processing	Polymerization	In this process, objects will print by photopolymerization. In photopolymerization liquid polymer will expose to light source to cure liquid into solid	*Better finish *Fast technique	*Price of set up is high *Post processing time especially detaching the object from machine is high	Polymers: UV-curable Photopolymer resin Resins: Visijet range (3D systems)	10 μm *DLP: 35-100
	Material Jetting		* Smooth Curvatures Printing * Multi-Jet Modelling Project	Inkjet	In this process material is jetted on the substrate to build 3D object	*Less wastages *Can develop FGMs with colour by single run	*Not always suitable for structural parts *Post processing is necessary	Polypropylene, HDPE, PS, PMMA	5–200 μm
	Binder Jetting		*3DP- 3D Printing *ExOne	Inkjet, binder, UV curing	In this process used binders are utilized. Binder acts as adhesive between powder and layer to create 3D object	*Process is generally faster than others *No melting	*Lower mechanical properties *Additional post processing	Metals: Stainless steel Polymers: ABS, PA Ceramics: Glass	13–16 μm
	Material Extrusion		*FFF - Fused Filament Fabrication *FDM- Fused Deposition Modeling	Melting, freezing filaments	This process utilizes filament of polymer, thermoplastic, or other material and extrude it through nozzle to print the object	*Less costly *Good mechanical properties	*Less accurate *Nozzle design issue	Polymers: ABS, Nylon, PC, PC, AB	50–200 μm
	Sheet Lamination		*LOM - Laminated Object Manufacture *SDL - Selective Deposition Lamination	Sheet joining	This process utilizes adhesives to form a bond between layers to print the 3D object by layer by layer.	*Inexpensive process *Good accuracy	*Limited material use *May need post processing	Paper, plastic and some sheet metals.	Variable
	Powder Bed Fusion (PBF)		*DMLS- Direct Metal Laser Sintering *SLM- Selective Laser Melting *SLS - Selective Laser Sintering	Melting, solidification of powder	With the help of laser or electron beam to melt or sintered the powder to form 3D object.	*Costly *Generally used for prototypes	*Lack of structural properties in materials *Size limitations	SHS: Nylon DMLS, SLS SLM: Stainless Steel, Titanium, Aluminium	80–250 μm

(*continued on next page*)

Table 1 – (continued)

Process and its line diagram		Commercial Models	Main Principle	Working Principle	Strength	Limitations	Typical Materials	Printing Resolution
Direct Energy Deposition (DED)		*LENS- Laser Engineered Net Shaping *LMD - Laser Metal Deposition *DMD- Direct Metal Deposition	Direct energy melting	Material melt by the energy source like laser or arc etc. and solidify to print the object.	*manipulate the grain structure *Very precise	*need to be explore more *Limited material use	Metals: Cobalt Chrome, Titanium	250 μm
Hybrid		AMBIT- Created by Hybrid Manufacturing Technologies	Additive and subtractive manufacturing	This process combines the AM principles with additional heating source as per demand to print the 3D object.	*Suitable to reduce the cost of object *Better accuracy	*Production costs are high *Comparatively slower process	Carbon fibre Nylon 12 Epoxy resin	

metal AM techniques have become epicentre of interest both for researchers as well as industry personnel [177]. Metal parts fabricated by AM route are found to increasingly meet the challenging distinct and functional demand of critical industries like automotive, defence, aerospace, constructions, electronic industry, etc. [178–182]. Wohler report [22,23] brings into the world's information that commercial AM systems sellers were 97 in 2016 and 49 in year 2014, out of which 49% were involved with metal AM systems.

PBF and DED are two main commercial metal AM techniques [183–185]. These technologies generally utilize powder as feedstock material. However, wire based feedstock materials are also utilized in DED techniques. These systems selectively melt metallic powders for part fabrication. A few upcoming AM techniques like friction based AM techniques [51,127,186–188], cold spraying [189–191], binder jetting [118,192], welding based AM techniques [40,193–199], hybrid AM techniques [200] etc. are gaining massive popularity amongst researchers and their industrial use is also growing with time.

In a broader perspective, depending upon the type of feedstock material and source of energy, AM techniques for metallic materials can be categorized as illustrated in Fig. 13.

Metallic materials such as titanium, alloys, steels, some grades of light weight metal alloys (Al and Mg), Ni based alloys, etc. are highly compatible with AM systems [141,202–205]. Subsequent section provides an insight into these metallic materials one by one.

3.3.1. *Ferrous alloys*

Different types of steels (austenitic, precipitation hardened, martensitic, duplex, etc.) are widely used ferrous alloys and are processed via PBF-laser and DED-laser AM techniques. Grades of austenitic stainless steels include 304-, 316-, 304L, 316L AISI type are most commonly used [206–210]. AM produces fine grained steel components as compared to conventional manufacturing techniques owing to rapid solidification along with non-equilibrium conditions [201,211,212]. Heat treatments are generally applied on AM produced steels to achieve desirable properties.

3.3.2. *Titanium alloys*

Titanium alloys are one of the most commonly researched AM materials. These alloys have excellent properties in terms of high strength to weight ratio, good fracture and fatigue resistance, good corrosion resistance and formability, etc. owing to which it is widely utilized in aerospace, automobile and bio-medical sectors [213–218]. Various researchers have reported the fabrication of titanium components using different AM techniques such as PBF and DED [78,141,219–221]. One of the most popular titanium alloys used for part fabrication via AM route is Ti–6Al–4V [221–227]. Main reason behind its extensive usage lies in its compatibility with numerous biomedical applications. Titanium has two phases in its pure form which are commonly referred to as α and β out of which the prior phase is strong with less ductility while the latter is more ductile. Alloys that have both these (α+ β) phases possess high strength and formability. These two phases can be carefully adjusted to achieve required properties in Ti alloys. To utilize them as bone mimics, the part density needs to be matched to

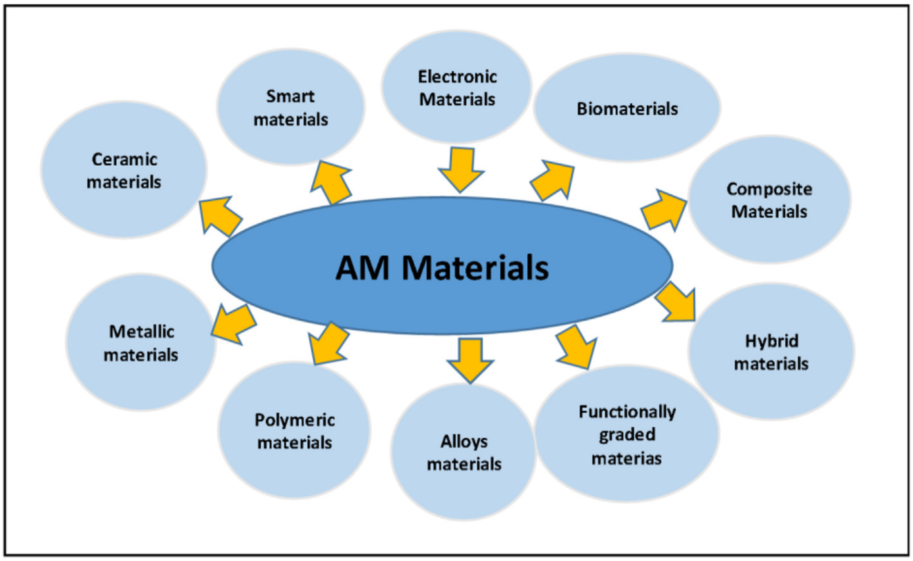


Fig. 9 – Classification of AM materials [2].

neighbouring material which is normally on the higher thereby requiring greater β phase content. As an alloying element, Al stabilizes α and V stabilizes β phase in Ti–6Al–4V alloy. Lesser stable α phase is formed when β phase is quenched. Hence, during fabrication of Ti–6Al–4V alloy parts, careful selection of printing environment specially (α+ β) phases to achieve required properties like strength, ductility, density and corrosion resistance.

3.3.3. *Aluminium alloys*

Aluminium (Al) alloys are widely utilized in various engineering sectors owing to their good strength to weight ratio and corrosion resistance. AM of Al alloys is still limited owing to poor weldability and low laser absorption of Al alloys [201,228–233]. Other reason may be understood as: Al alloys gets melted during the fusion based AM process there are more chances of solubility of hydrogen and with subsequent solidification of melt pool, hydrogen gets entrapped which leads to formation of pores. These solidification related defects weaken the mechanical properties of the manufactured part. To avoid these issues the process zone should be shielded using additional shielding gas [234]. In addition to DED and PBF other indirect AM processes such as arc welding based AM processes [235,236] and newly developed solid state

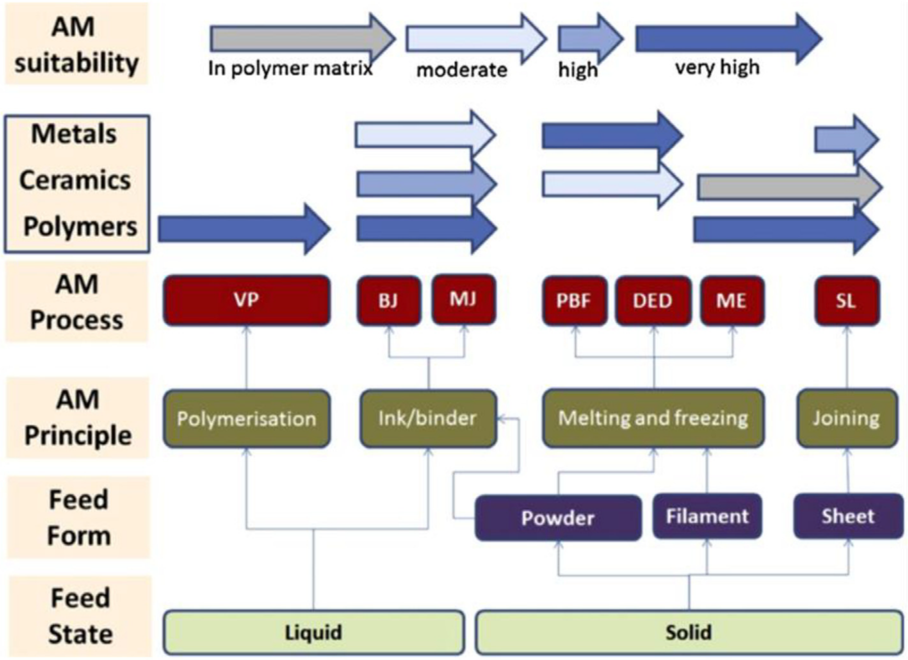
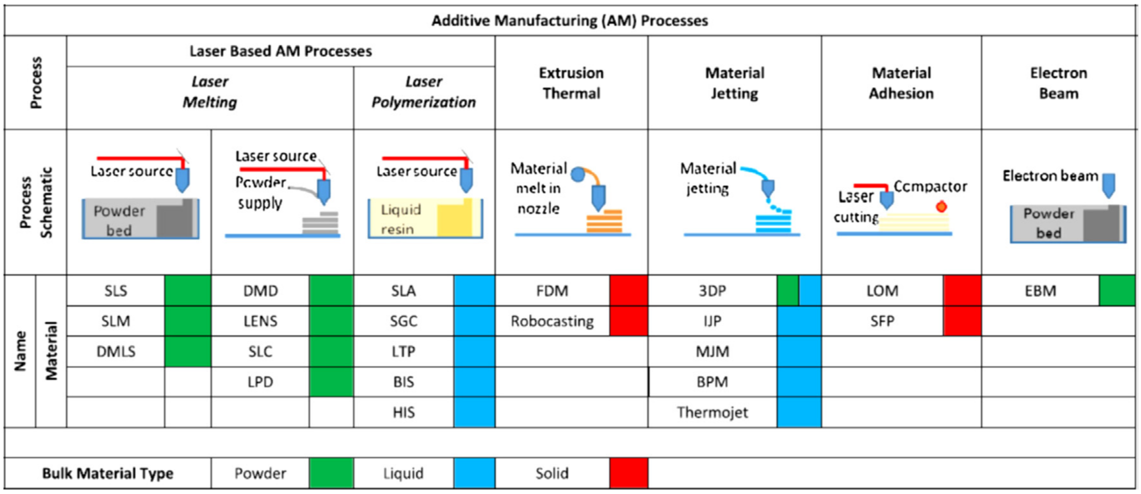


Fig. 10 – Suitability of AM techniques (for seven categories of AM as per ASTM classification) of polymers, metals and ceramics in different feed forms/states [155].



Additive Manufacturing (AM) Processes							
Process	Laser Based AM Processes			Extrusion Thermal	Material Jetting	Material Adhesion	Electron Beam
	Laser Melting		Laser Polymerization				
Name / Material	SLS 🟩	DMD 🟩	SLA 🟦	FDM 🟥	3DP 🟩🟦	LOM 🟥	EBM 🟩
	SLM 🟩	LENS 🟩	SGC 🟦	Robocasting 🟥	IJP 🟦	SFP 🟥	
	DMLS 🟩	SLC 🟩	LTP 🟦		MJM 🟦		
		LPD 🟩	BIS 🟦		BPM 🟦		
			HIS 🟦		Thermojet 🟦		
Bulk Material Type	Powder 🟩		Liquid 🟦	Solid 🟥			

Fig. 11 – AM categorization on the basis of form of materials [156].

AM techniques such as friction based AM techniques [237–242], etc.

3.3.4. *Magnesium alloys*

Magnesium alloys are promising materials for use as a degradable biomaterials having similar stiffness to bone which can minimize the stress shielding effects [243]. The applications of Mg alloys are increasing at a rapid rate including orthopaedics [244–246], urology [247], cardiology [248], respirology [249], etc. AM of Mg alloys is attracting interest owing to their ease of design as compared to traditional manufacturing techniques. AM has capability to develop biodegradable implants. Several AM techniques such as powder bed fusion [250,251], laser AM techniques [252], wire-arc AM [253–255], friction stir based AM [51,256,257], etc. are utilized for development of Mg alloy based biodegradable materials. These AM processes have different process mechanics and forms of raw material. Some of these AM processes such as PBF (SLM, EBM) are facing problem of oxidation and evaporation of Mg during processing [250]. However, this difficulty can be overcome by printing Mg alloy in inert atmosphere with optimized process parameters. In such cases in-direct AM processes are playing an important role in developing biodegradable Mg alloys [257].

3.4. *AM of ceramic materials*

A few raw materials like ceramics and concrete have limited utility in AM owing to the fact that their discrete particles are unable to fuse together by heating them up to their melting points [258]. On the other hand, polymers and metals sufficiently fuse at their melting points. Also, ceramics have appreciably higher melting points as compared to polymers and metals which is a major challenge before AM processes. Thus, AM techniques that have the ability to fabricate ceramic parts impart them mechanical properties which are comparable with those manufactured using conventional manufacturing processes [259–265]. PBF based AM processes are especially suitable and economical methods to develop ceramic parts but limitation on availability of initial raw materials for obtaining feedstock is still a challenge in AM of ceramics. Ceramics such as calcium phosphate, silicon

Table 2 – Single step AM processing for different AM materials (metal, polymer and ceramic).

Type of material	State of fusion	Material feedstock	Material distribution	Basic AM principle	AM Process Category
Metallic	Molten state	Filament/wire	Deposition nozzle	Selective deposition of material	DED
	Solid + molten state	Powder	Powder bed	Selective fusion of material on a bed	PBF
	Solid state	Sheet	Sheet stack	Fusion of stacked sheet	SL
Polymer	Thermal reaction bonding	Filament/wire	Deposition nozzle	Extrusion of melted material	ME
		Melted material -liquid	Print head	Multi-jet material printing	MJ
	Chemical reaction bonding	Powder -Printhead	Powder bed	Selective fusion of material on a bed	PBF
		Liquid material	Print head Vat	Curing (reactive) Curing by photopolymer by light	BJ MJ VP
		Sheet	Sheet stack	Fusion of stacked sheets	SL
Ceramic	Solid state	Powder and liquid suspension	High density green compact	Selective fusion of particles in a high density green compact	PBF
	Solid + liquid State	Powder material	Powder bed	Selective fusion of particles on a bed	

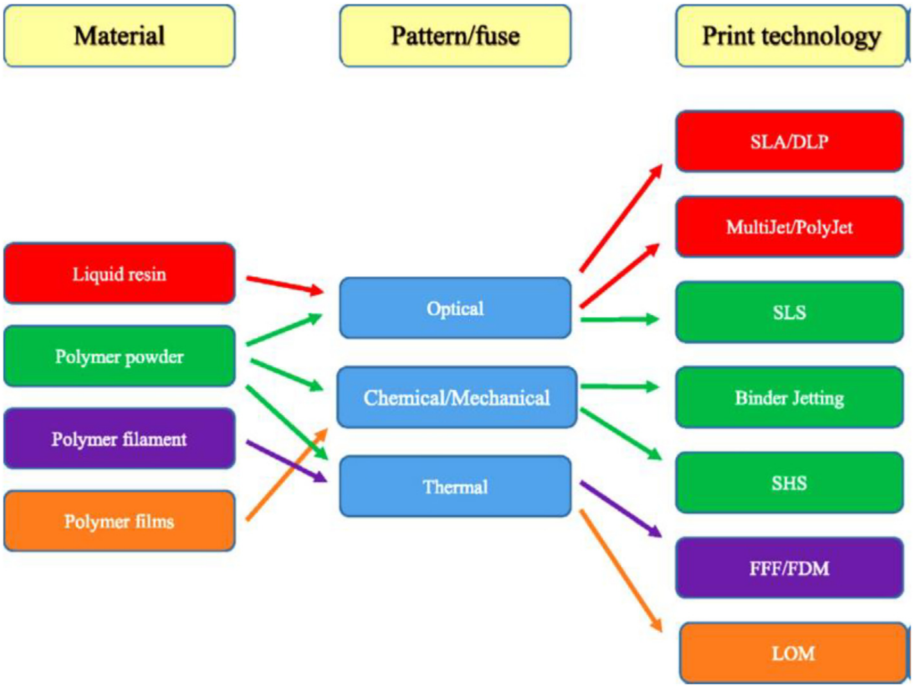


Fig. 12 – Overview of polymers/monomers used in additive manufacturing [168].

carbide, silica, etc. are commonly processed using PBF [68]. Ceramic materials have several applications in different sectors such as in aerospace, automobile (in development of engine and propulsion components), electronic components, microchips, etc. [266]. One of the most promising applications of ceramics AM is in tissue engineering and biomaterials. Sintering and post processing in ceramics requires extra time and makes the process quite expensive. However, this does not lessen the attractiveness of these AM processes for fabrication of intricate shaped components. A very special example of ceramic AM parts are scaffolds made of ceramics for bones and teeth. This is an integral part of tissue engineering since the process is relatively fast in comparison to traditional processes like casting or sintering.

Apart from PBF, AM techniques like stereolithography, paste extrusion, LOM and inkjet (suspension) are also commonly used [267–278]. SLS is commonly applied for ceramic parts via AM route but cracking is a common sight in SLS parts which can be attributed thermal shocks of heating and cooling in the course of processing [279,280]. Layered appearance in the AM printed parts is yet another concern. In few applications like biomedical or tissue engineering, this may not very critical. However, this is a serious limitation in applications like aerospace, construction, etc, where planar external surfaces are mandatory otherwise stress accumulation at selective points may start. This defect is illustrated in Fig. 14.

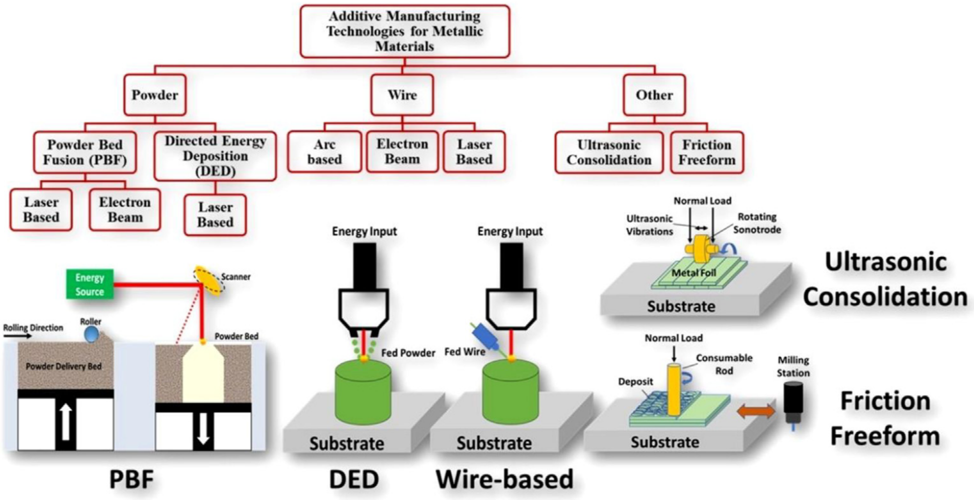


Fig. 13 – Categorization of different AM techniques depending on form of feedstock and process of fabrication: (a) PBF; (b) DED; (c) Wire-arc AM; (d) ultrasonic AM; (e) friction based AM [201].

Fig. 14 – Layered appearance defect in concrete structure obtained via AM route [281].

3.5. *AM of cermets*

Cermets are basically combination of metallic and ceramic phases which offer combined properties of both ceramics and metals. In cermets, ceramics are basically in the form of reinforcement phase while metals are in the form of binding phase. Oxides, carbides, nitrides and carbonitrides of tungsten, titanium, tantalum, etc. while molybdenum, nickel alloys, etc. are generally used as metallic binder [282,283]. Cermets find various applications in forming, cutting, etc. Cermets are fabricated using several conventional methods such as powder metallurgy, mechanical alloying, spark plasma sintering, hot pressing, casting, plasma spraying, laser techniques, etc. [282,284–286]. Recently, AM is being considered as attractive process for fabricating cermets. SLS/SLM [287–290], LENS, binder jetting, direct laser deposition, etc. are major AM techniques which are used for development of cermets [282]. Also, direct ink writing [291], 3D gel printing [292], etc. are recently utilized for fabrication of cermets. Fig. 15 shows some samples of cermets fabricated via different AM techniques.

3.6. *AM of composite materials*

Composites are an exclusive class of materials and are newer than polymers or metals. Composites can be understood as combination of more than one (two or more than two) constituents with final properties appreciably different as compared to its constituents [296–298]. A few AM have the capability of composite parts fabrication that have substantially enhanced properties as compared the base constituents. This has made fabrication via AM processes quite popular. Various AM techniques are used for fabrication of composites [299–303]. Each technique offers different suitability depending upon the base matrix (metal, polymer, ceramics) and reinforcement particles [304–319]. A few issues in processing of composites especially dense metal matrix composite material using fusion based AM techniques are gas entrapment, stress development, gaps between base matrix and reinforcing particles, etc.

Table 3 presents an overview of processing of metals, ceramics and composite and their suitability with AM processes.

3.7. *AM of smart materials and structures*

There is more than one school of thought regarding the definition of the smart materials. One of them defines smart materials as a special class of materials that can convert energy from one physical domain to the other [320,321]. Others define them as materials that generate productive output as a response to environmental changes by modifying their geometry/property [322]. Both of the approaches are equally

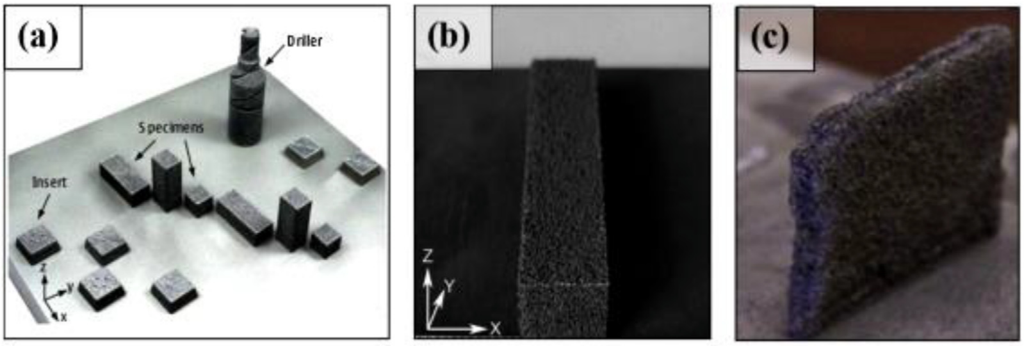


Fig. 15 – Examples of Cermets fabricated via [282]: (a) SLM [293]; (b) direct laser sintering [294]; (c) LENS [295].

Table 3 – Multi step AM processing for different AM materials (metal, ceramic and composite).

Type of intended product material	Principle of adhesion	Material feedstock (bonding/bulk)	Material distribution (bonding/bulk)	Basic AM principle	Process Category	Consolidation Through secondary processing
Metallic, Ceramics and Composites	Bonding due to thermal reaction	Composite sheet material	Sheet stack	Joining of stacked sheet	SL	Furnace sintering, with or without infiltration
	Bonding due to chemical reaction	Particle/powder, metal/ceramic powder	Powder Bed	Selective fusion and bonding of material	PBF	
		-Liquid, thermoplastic	-Printhead -component in the bulk	Reactive curing	BJ	
		Liquid/powder	Vat	Light reactive photo-polymer curing	VP	

utilized in practise. As per Pie [1,13], 4D AM is "the process of building a physical object using appropriate additive manufacturing technology, laying down successive layers of stimuli-responsive composite or multi-material with varying properties. After being built, the object reacts to stimuli from the natural environment or through human intervention, resulting in a physical or chemical change of state through time". As per Tibbits [14], 4D AM is a process that "entails multi-material prints with the capability to transform over time, or a customised material system that can change from one shape to another, directly off the print bed" with "the fourth dimension described here as the transformation over time, emphasising that printed structures are no longer static, dead objects; rather, they are programmably active and can transform independently".

In general, it can be concluded that smart materials are an exquisite class of materials which possess capability of changing shape or property when subjected to some external stimulus. They have a special ability to structurally reconfigure themselves. This gives rise to a new concept of 4D printing since a new dimension of shape/property/structural reconfiguration [12]. The structures/parts obtained using smart materials thus have capability to evolve with passage of time. These processes are therefore called 4D AM techniques [12,323–326]. An important point that demarcates the 4D AM from its 3D version is its capacity to demonstrate self-actuating, shape-changing and sensing behaviour. PolyJet 3D printing [48,327] and SLM by Stratasys and SLM solutions respectively are the two main game changers in the direction of 4D AM. However, many other AM techniques are also nowadays being increasingly used to obtain 3D printed smart objects or 4D enabled objects. These objects are classified based upon the utilization of single or multiple smart materials for their fabrication. In the first case when either a smart material is either singly utilized or it is combined with other conventional materials, the adaptive, sensing, decision making, functionality, and shape memory smartness of the smart material plays the most important role [328–330].

3.8. *AM of shape memory alloys*

Shape memory alloys (SMAs) have potential of remembering their original shape after deformation and this effect is termed as shape memory effect [331–333]. Owing to their unique inherent characteristics, SMAs are suitable for applications in various engineering sectors such as aerospace, automotive, biomedical and scientific applications [334–337]. There may be various kinds of shape memory materials as reported by Zafar et al. [323] (see Fig. 16). One of the important SMAs is Ni-Ti alloys and considered as superior to other SMAs such as Cu-based and Fe-based alloys owing to its higher strength, ductility and refined grain structure [338,339]. Ni-Ti alloys are biocompatible also, owing to which around 80% of products made up of these SMAs are medical related [340]. Additionally, these are highly useful in actuators of stress-creating components. One of the major issues during traditional manufacturing of Ni-Ti alloys is their poor machinability. Owing to which tube and wire drawing are the major forming techniques for developing devices such as stents, actuators,

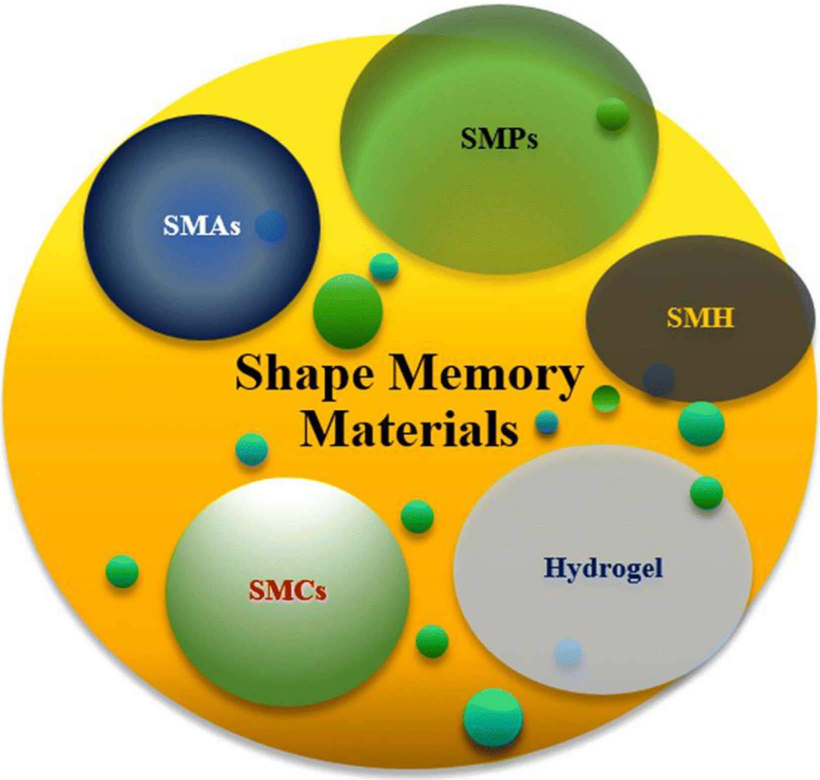


Fig. 16 – Different types of shape memory materials for AM [323] (where, SMAs: shape memory alloys; SMPs: shape memory polymers; SMH: shape memory hybrid; SMCs: shape memory composites).

guise wires, etc. [338] that limits their use for complex shapes. In this regards, AM is gaining popularity in developing Ni-Ti alloys based devices in medical as well as other sectors. Out of different AM techniques, laser-based processes, especially L-PBF, is one of the major approach for developing Ni-Ti and considerable research work has been reported over laser based additive manufacturing of Ni-Ti by various researchers [231,332,341–349].

4. Binding mechanisms in AM

It is a matter of clear understanding that the AM parts are fabricated in layers which are joined to each other by some means. The mechanism, extent and efficiency with which bonding of layers occurs chiefly decides the output effectiveness and success of any given AM technique [350]. Also, each AM process/system has a unique binding mechanism to bind the layers [351,352]. It is thus imperative to understand the various binding mechanisms in AM. Additionally, binding mechanisms have been utilized to classify some of the AM techniques especially SLS and derived technologies in a few research works [76,353]. A non-exhaustive indicative approach is to divide these AM binding mechanisms broadly in four classes as shown in Fig. 17 [354], which mainly include:

- Secondary phase assistance binding mechanism
- Chemical induction binding mechanism

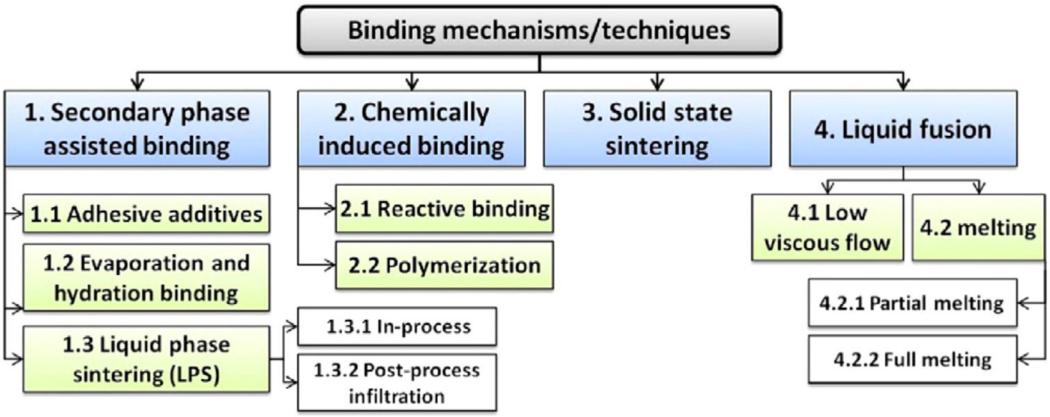


Fig. 17 – Indicative classification of AM binding mechanisms [354].

- Solid state sintering binding mechanism
- Liquid fusion binding mechanism
- Melting based binding mechanism

4.1. *Secondary phase assistance based binding mechanism*

AM processes like sheet lamination, SLS, binder jetting, etc. are based on utilizing binding layers mutually with the aid of secondary phase [355]. This secondary phase can be liquid, coating, powdered material, etc. Nozzles, coatings, etc, are utilized to add the secondary phases and layers are bonded chiefly with the aid of adhesive materials, liquid phase sintering, as well as evaporation and hydration [356].

Sheet lamination and binder jetting use adhesive bindings. Addition of adhesives in liquid of dry state to the main material is accomplished either by automatic nozzles or embedding them in powdered bed. The binder in dry form reacts with already deposited powder after it to powder bed. On the contrary, liquid binders consists binding material. Coatings are directly applied and subsequently layers are bonded by applying heat and/or pressure in case of sheet lamination.

4.2. *Chemical induction based binding mechanism*

Secondary phases are not required to accomplish binding in case of chemical induction binding. Processes like vat photo polymerization, material jetting, SLS, etc. are based on utilizing chemical reactivity of material to bind layers [355].

4.3. *Solid state sintering based binding mechanism*

Solid state sintering is performed at temperatures below melting point of the material and comes under the class of thermal consolidation processes [355,357]. It is based on diffusion binding and is used for post processing. Various physical and chemical reactions take place during solid state sintering. Neck is formed due to atomic diffusion within and this tends to become bigger with time. This process is most suitable for ceramics.

4.4. *Liquid fusion based binding mechanism*

Most of the AM processes are based on mechanism of liquid fusion binding. In this mechanism, low viscosity flow occurs in polymers but melting takes place in metals [358]. The subsequent layers fuse upon deposition over previous layers during low viscosity flow. A few examples include droplets of wax in material jetting process, deposition of heated polymers upon previous layer in powder bed fusion, etc.

4.5. *Melting based binding mechanism*

This method of binding layers involves partial and full melting during binding and is mainly applicable for metals and SLS of polymers [359,360]. Metal is partly melted and is available as a mixture of solid metal along with molten metal between solid layers/particles in case of partial melting [361]. On the other hand, perfectly dense parts are obtained in case of full melting resulting in elimination of any requirement for post-processing densification. Hence, binding by melting is responsible for fabrication of dense metallic parts obtained in case of DED and PBF techniques [358,362].

5. Challenges in AM materials

Modern world has witnessed tremendous progress in AM research and consecutively in its applications as well as advancements. However, there are numerous challenges that

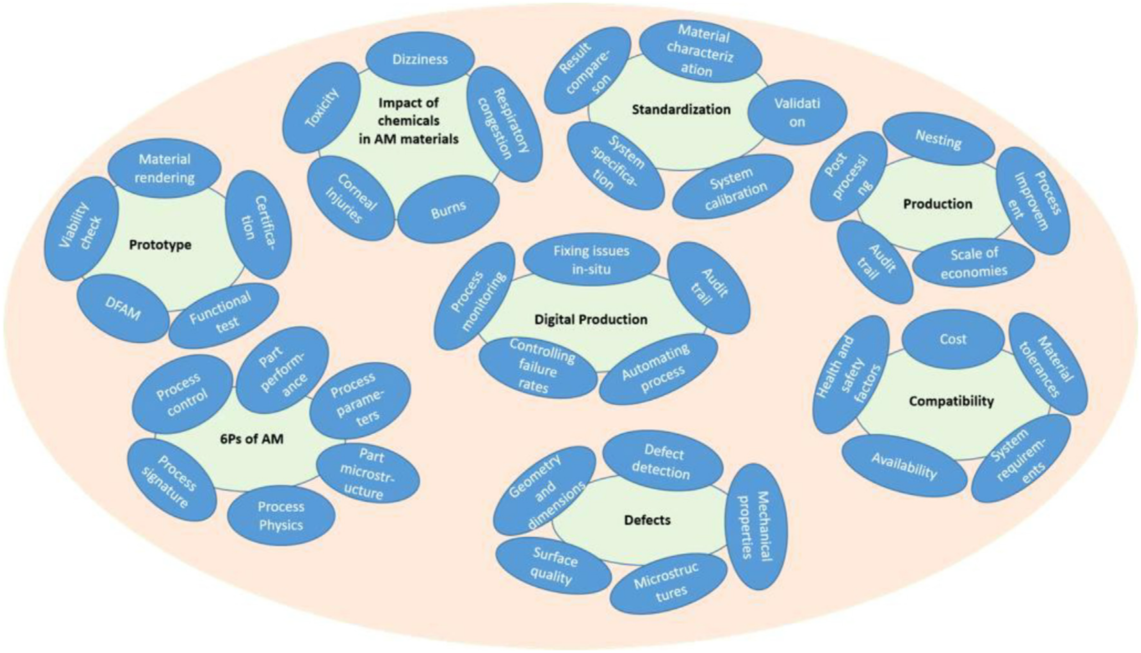


Fig. 18 – Challenges of AM materials.

need to be overcome completely to enable utility of AM as TL4 level technology and enable its metamorphosis from research labs to real life industries [212,363–367]. One main issue is the compatibility of raw materials with AM processes. The restraint due surface finish, dimensional accuracy, anisotropic behaviour, etc. of the parts fabricated is another challenge faced by AM materials. Yet another challenge is the lack of testing facilities for specific parts and materials fabricated via AM route. One most important challenge is the occurrence of several defects in parts fabricated by AM techniques. The other challenges related to AM materials are illustrated in Fig. 18.

Some of the common defects are discussed in subsequent sub section.

5.1. *Defects in AM parts*

Many of the advanced and upcoming AM processes are more of less at development stage and the relation between material properties and process parameters is not fully understood. Owing to this lack of understanding, occurrence of defects is quite prominent. Occurrence of defects leads to inferior mechanical and other properties of the fabricated parts [368–372]. A brief overview of commonly occurring defects in AM fabricated parts is presented in the following section.

5.1.1. *Balling phenomena*

The balling phenomena also called as bead up is a defect where underlying surfaces are not wetted by liquid material and results in occurrence of beaded scan track thereby increasing surface roughness as well as tendency to form pores [69,373]. This defect mostly occurs in AM processes that are based on laser sintering based. Fig. 19 presents an illustrative example of occurrence of this defect.

5.1.2. *Porosity*

Porosity Most of the binding mechanisms are associated with temperature variations under capillary action and gravity without the aid of external forces. A few causes for porosity/void defect is recurrence of keyhole emergence, gas entrapment leading to microscopic pores during atomization, insufficient penetration of subsequent layers into substrate, etc. [375,376] Fig. 20 presents an illustration of this kind of defect. Keyhole pores have size less than hundred microns.

5.1.3. *Cracks*

Another commonly occurring defect in parts fabricated by fusion based AM processes are cracks since metals swiftly melt and solidify during these processes [378]. Owing to this fast cooling, large temperature gradients and correspondingly large thermal residual stresses generation occurs. Large residual stress when combined with high temperature gradient lead to crack initiation. Cracks are especially prominent along grain boundaries since temperature varies for each layer, i.e., substrate, solidifying and deposited because of varied contraction rates [53]. In mushy zones, liquation cracking [52] is a common defect since these zones are subjected to tensile forces that lead to initiation of cracking at liquid films [53]. Similarly, other cracks can be understood. If residual stress at interface is greater than yield strength of alloy, mutual separation of layers or delamination occurs.

5.1.4. *Distortion*

Distortion defect occurs in AM parts if stress development takes place in material owing to volume shrinkage [379–381]. An illustration of this distortion defect is presented in Fig. 21.

5.1.5. *Inferior surfaces*

Inferior surface is a predominant defect in AM parts and is chiefly attributed to staircase effect. A few other contributory factors are part build orientation, rough bead deposition (example, in FDM), limited tool precision (example, in EBM),

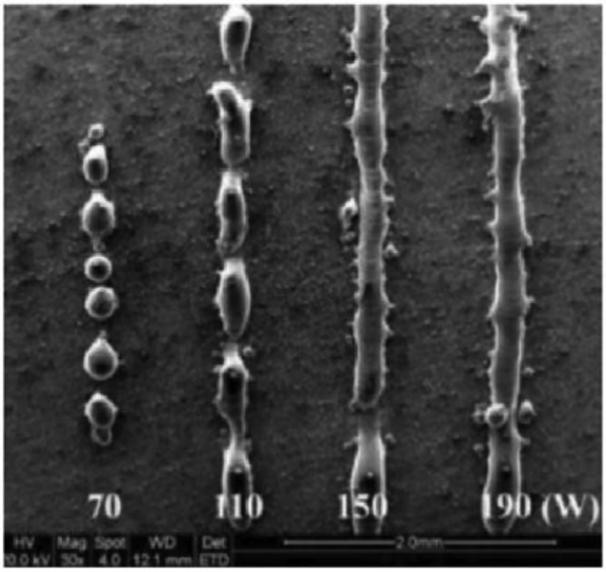


Fig. 19 – Balling defect at low laser power (SLM of 316L stainless steel) [374].

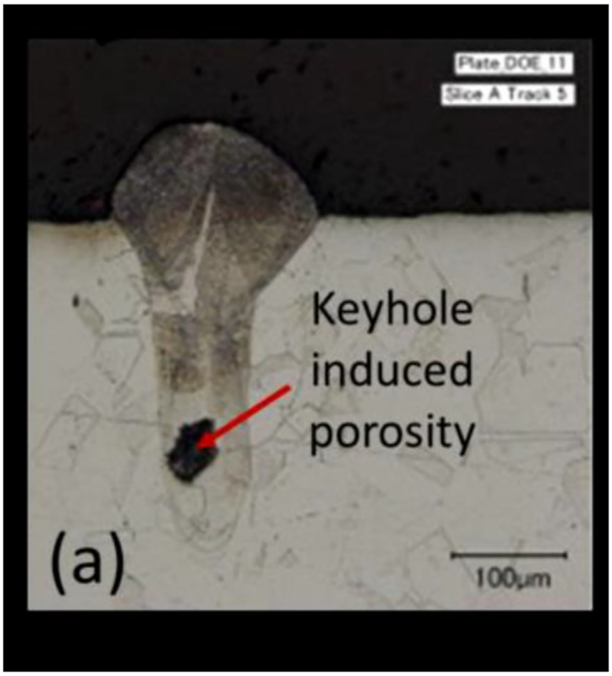


Fig. 20 – Porosity defect (keyhole porosity) during MAM [377].

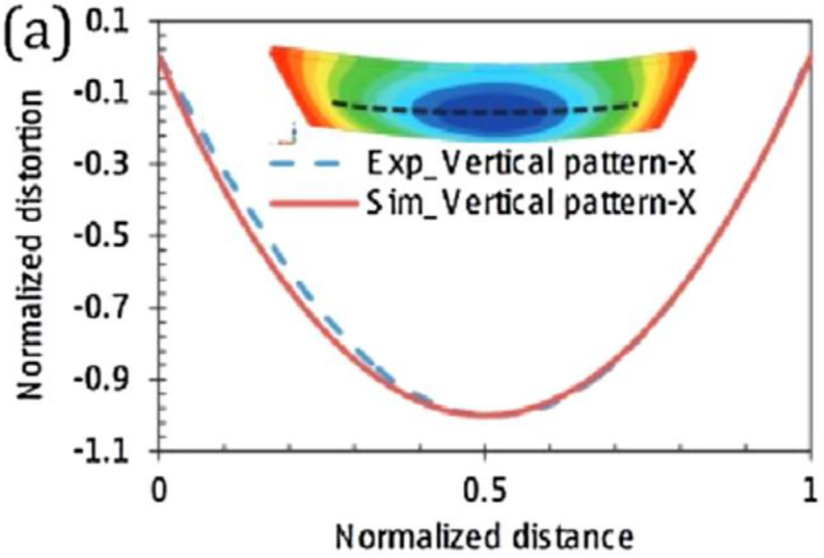


Fig. 21 – An illustration of distortion defect in SLM processed steel [382].

surface tension and balling (example, in PBFs), semi-molten powder (example, in SLM), use of aged material (example, in SLS) etc. are also responsible. Better surfaces can be obtained if all these process specific challenges are overcome. It is observed that attempts to reduce surface roughness leads to lower production rates and higher production costs. This is chiefly because of increased requirement of processing time and post processing requirement.

5.2. *Limitation on size*

Maximum size of the part that can be fabricated via a particular AM process is limited by the size of the build volume of the given AM machine set up. Large sized parts require even larger printers. This puts additional requirement of space. An alternative approach can be to fabricate large sized parts in segments and then assembling the segments which increases time requirement.

5.3. *Production speed*

Present day AM techniques are more suitable for job order flexible automation only. However, mass production is still a challenge and traditional methods are best suited for such applications [383,384].

5.4. *Initial investment*

A huge capital investment is in general required for industry grade AM equipment. It is true that the costs have tremendously reduced over past few decades but still it is much higher as compared to traditional equipment. The cost of raw materials is also high and there is a restraint on their compliance and availability [385–388]. Significant ongoing efforts are focussed towards research in direction of reduction of material cost for AM process.

6. Critical analysis and future outlooks

Enhancing the performance of materials is always an area of research for conventional as well AM techniques. Considerable research on materials for AM has been reported. However, the materials development for AM processes is facing some challenges. Anisotropy, mass customization, microstructural control, compositional control, variety, etc. aspects remain some major restraints upon the AM materials. Lack of regulatory issues is also a problem area that needs focus to broaden the spectrum of AM raw materials and corresponding legal as well as social compliance. One of such challenge is availability of raw material for different kinds of AM fabricators. Another main challenge includes the characteristics of smart materials or composites. One such example is shape memory alloys (SMAs) especially NiTi SMAs. These alloys need great efforts to be fabricated by AM techniques owing to their compositional sensitivity. These alloys are prone for microstructural defects, phase change, oxidation, etc.

A significant research work on AM techniques has been reported. However, there are several challenges in realizing their realistic impact. This is mainly owing to the fact that AM research is fragmented due to large variation and representations in AM methods. Due to this fact the repeatability is quiet difficult in AM techniques. Repeatability and consistency are major factors for a manufacturing process to be adopted by industries. In case of AM, these are required for different machines/fabricators of same model, in-between builds and build volume of each machine. Also, the mechanical and other properties of fabricated parts are not good and consistent owing to which many industries are not sure whether they will match the specification of build AM parts according to the need. One of the major reasons for this issue is predominance of rapid prototyping machine architectures for AM systems. In addition, a lot of research efforts are needed further to develop new materials, novel AM techniques, new fabricators, etc. for different engineering and medical applications. The suitability of newly developed systems for AM Targets should be set to develop newer grade materials for AM.

7. Conclusions

Materials play an important role in AM processes. At present polymers, ceramics, composites, metals, alloys, functionally graded, smart and hybrid materials, etc. are widely utilized AM raw materials. Raw material should have compatibility with the particular AM machines. For most of the innovative AM applications, rigidity in the choice of raw materials is a key challenge. Functionally graded materials and hybrid materials offer some respite to these issues. Poor mechanical performance, high cost, lack of suitable machine availability, health hazards associated with several materials, limitations on testing as well as standardization and material characterization techniques, etc. are some aspects related to currently available raw materials that restrain full exploitation of AM technology. Understanding the physics behind binding mechanisms associated with materials corresponding to different AM techniques is a prerequisite in understanding the process dynamics. Techniques to improve mechanical and microstructural properties, ways to develop specially engineered materials, recycling of AM materials, significance of particle size and distribution of material, exploring thermal issues, synthesising newer materials especially for customised in-house applications, developing a material database, etc are some important research areas related to the AM materials. These issues need serious consideration especially when fabricating parts for key industries like biomedical, construction, aerospace, automotive, etc. As discussed in this article, though several researchers have reported work in this direction, a lot still remains to be accomplished and several technological and scientific aspects need careful attention in this direction. To conclude, there is a long way to go before all the raw material aspects are fully addressed and hence several research avenues lie unexplored in this crucial aspect for the full scale utilization of AM technologies.

Declaration of Competing Interest

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

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