Materials Horizons: From Nature to Nanomaterials

Shashanka Rajendrachari *Editor*

Practical Implementations of Additive Manufacturing Technologies

Springer

Materials Horizons: From Nature to Nanomaterials

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Shashanka Rajendrachari
Editor

Practical Implementations of Additive Manufacturing Technologies

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Foreword

Dear Readers,

The present book entitled *Recent Advancements in Additive Manufacturing: Synthesis, Properties and Applications* is very informative and one of the simple, best books on additive manufacturing I have come across. This edited book includes the fundamentals of additive manufacturing to synthesise and applications of various alloys. All the authors of this edited book are well experienced in additive manufacturing, and I congratulate all the authors of the book for their excellent contribution.

This book is comprised of a total of 16 chapters. Chapters 1 and 2 of this book provide basic details of additive manufacturing such as the history, recent developments, challenges, design and materials selection for the processes. Chapter 3 discusses the synthesis of nano-structured materials by additive manufacturing techniques followed by a discussion of their properties and applications. The next chapters from 4 to 7 discuss metal, biomaterial, composites and smart materials-based additive manufacturing, respectively. Chapters 8 and 9 focus on electrical and electrochemical properties like 3D printed batteries, supercapacitors, and electrochemical and biosensor applications of additively manufactured materials. Chapters 10–13 explain the applications of additively manufactured materials in the automobile, medical, sports and construction sectors. The remaining chapters are unique and rare and may not be available in most of the additive manufacturing books. These chapters discuss the environmental impact, future perspectives, economic impact and the kind of jobs available in additive manufacturing industries.

Prof. Dr. Yusuf Usta
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Preface

The field of metallurgy is evolving every year with newer technology and improvement in the grades of alloys. One such modern technology is additive manufacturing. The idea of drawing something on computers and bringing the same structure to physical form with perfect dimensions was a joke in the last few decades, but now it is possible to manufacture complex structures using a 3D printer, Thanks to the additive manufacturing technique. The field of additive manufacturing has witnessed extraordinary growth both industrially and academically due to its wide range of benefits. But still, researchers are improving the technological lacunae and preparing complex structures with different grades of alloys. Our main aim is to throw light on the recent development in additive manufacturing technology.

This book comprises 16 chapters authored by various pioneers of additive manufacturing from different countries. This book gives in-depth information about the evolution of additive manufacturing from a few decades to the present. It also explains how the technology has been improved with time: the different types of additive manufacturing methods used to prepare materials and their advantages, followed by the limitations. The synthesis of nano-structured materials using additive manufacturing techniques and the detailed discussion of their properties and general applications are included in this book. The fabrication of metal, biomaterial, composites and smart materials using additive manufacturing methods are also explained along with their special properties. This book also comprises additively manufactured 3D printed batteries, supercapacitors, electrochemical sensors, biosensors, automobile components and medical implants. The advanced applications of additive manufacturing materials in the construction, biomedical and sports industries are also included. The environmental impact, the future and the economic contribution of additive manufacturing industries are discussed in this book. This book also contains a chapter on the general type of job opportunities for engineering graduates and research scholars in additive manufacturing companies. This book is mainly channelized for research scholars and engineering students to understand the basic concepts of additive manufacturing. This book also motivates students to choose additive manufacturing as their career because it provides sound knowledge about the job opportunities offered by various additive manufacturing companies. Ph.D. students who are working in the different areas of additive manufacturing could be more beneficial from this book. Engineering students (bachelors and masters) studying in departments like mechanical engineering, metallurgical and materials engineering are the targeted audience of this book. All the powder metallurgy companies especially their R&D sections could be benefitted by the proposed book. Nowadays, many universities are teaching powder metallurgy, additive manufacturing as one of the subjects in mechanical, ceramic engineering and metallurgical and materials engineering branches. This book can be used as a reference book for these courses all over the world. This book covers most of the basic additive manufacturing topics along with recent advancement and the general job opportunities for students. This book also gives information about the contribution of additive manufacturing companies to the economy of the country.

Bartin, Türkiye Dr. Shashanka Rajendrachari

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About the Editor

Dr. Shashanka Rajendrachari is currently working as an assistant professor in the Department of Metallurgical and Materials Engineering at Bartin University, Türkiye. He has completed post-graduation M.Sc. (Industrial Chemistry) and M.Tech. (Nanoscience and Technology) from Kuvempu University, Shimoga, India. Later, he obtained Ph.D. from the Department of Metallurgical and Materials Engineering at NIT Rourkela, Odisha, India, and possesses excellent interdisciplinary academic and research background; his area of interest includes mainly powder metallurgy, additive manufacturing, electrochemical sensors, nanomaterials, corrosion, etc. He has contributed 10 book chapters, eight books, and 60 International research publications. He is the reviewer and editor for many international journals published by Springer, Elsevier, MDPI, etc. He was awarded as the best powder metallurgy student of the year 2015 from powder metallurgy association of India at IIT Bombay and also awarded many international awards for research and teaching.

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Chapter 1
Recent Developments in Additive Manufacturing

Dervis Ozkan, Gulfem Binal, Garip Erdogan, Ahmet Gulec, Yasin Ozgurluk, Sefa Erdem Yilmaz, and Abdullah Cahit Karaoglanli

Abstract Additive manufacturing (AM), which emerged as an alternative method to traditional manufacturing methods such as casting and forging, holds many advantages, from 3D design to material selection to production. Researchers and industrial users have recently used the method in numerous application fields due to its outstanding properties in industrial use. Additive manufacturing technology is mainly used in many different industrial areas, such as aerospace, defines, biomedical, automotive, and energy. This study is divided into six sections, which include a literature review of Recent Advancements in Additive Manufacturing. The sections

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of the study consist of the history of additive manufacturing technology from the past to the present, additive manufacturing methods, used materials, general process workflow, industrial usage areas, and recent developments in additive manufacturing technology. The current study presents a roadmap for future research in additive manufacturing technology specific to synthesis, properties, and applications.

Keywords Additive manufacturing (AM) · 3D printing · Materials · Industrial applications · Recent developments

1 Introduction

The production of new materials in many industries globally increases the need for raw materials. The increase in the need for raw materials also brings about the production of new materials by using many underground and surface resources. For this reason, engineering applications are looking for new material production using alternative and innovative technologies [1–3]. The technology that has developed in recent years is the 3D production method. The 3D production method, which emerged towards the end of the 1900s, is known by the other name of additive manufacturing (AM) technology. Additive manufacturing, which remained only a research subject until the 2000s, has started to be used, especially in engineering fields, thanks to the widespread use of CAD, SolidWorks, and AutoCAD drawing programs and the decrease in printer prices, along with the developing technology [4–6]. The physical shape of a drawn object, thanks to the use of drawing programs directly, has aroused great interest in the field of production and left traditional manufacturing technologies behind. Moreover, one of the other advantages of the 3D production method is that it is inexpensive and fast [7, 8]. Additive manufacturing technology, which has been a groundbreaking innovation since its use in production, is a technique that provides layer-by-layer production, especially in the production of complex-shaped parts. This production technique is commonly characterized by low energy use and high design characteristics. Due to its advantageous production features, additive manufacturing is widely used in construction, dentistry, and other health sectors, especially in the aviation industry [9–12]. Another advantage of AM is that there is no need for molding tools as in other plastic forming methods, such as the casting method. This saves both time and money. Production of special parts can be done easily thanks to computer-aided design programs. This production method is bottom-up or top-down layer-by-layer production, unlike injection molding or casting production techniques [13, 14]. All polymer, metal, composite, and ceramic materials can be used easily in this production technique. The reason for the increase in interest in this technology is that all the manufactured products are of high quality and durable. The advanced computer software used determines the production of products with complex shapes by the 3D method as a research subject. In addition, thanks to this method, which is also evaluated in waste products, it is also a source of ideas for the production of new-generation composite materials. Thanks to the use of waste products that are harmful to the environment, materials that have not been lost in nature for centuries are re-evaluated in various industries [15, 16]. The new generation of complex-shaped parts is in high demand in the fields of packaging, automotive, aerospace, tissue engineering, and medicine [1, 17]. Synthetic plastic, a non-biodegradable waste, has begun to endanger the environment and ecosystem. The increasing number of problems in the environment arising from manufacturing techniques has led scientists to seek sustainable materials rather than synthetic polymers [2, 18]. The production of sustainable materials has also started to necessitate the transition to additive manufacturing, which is a layered production technique, by reducing the traditional production techniques of casting, injection molding, and compression molding [1, 19–22]. In line with this scope, it has been seen that it is possible to produce many bio-containing polymer-based materials from sustainable sources, but it has been understood that they do not decompose in nature. It has been seen that the AM production technique is the best method for collecting and evaluating polymer-based waste products and solving waste problems [1, 23–25]. 3D technology is an area where waste plastics with complex shapes can be evaluated, and synthetic plastic materials are mixed with materials such as biocarbon and cellulose to create a filler material [26–29]. In addition, AM is not only a production technique but also combines several technologies that have been developed in recent years. The material produced in traditional production methods is considered as a manufacturing methodology, which is removed from the mold [1, 30–32]. In AM technology, the materials are produced by adding them on top of each other. An aesthetic structure is created by adding the materials layer by layer. In terms of usage, the use of a material produced this way is very efficient. There are several different 3D technologies depending on where the materials will be used [1, 33]. The market size of 3D manufacturing technology is increasing day by day. These increases in market share are due to the researchers' efforts to integrate this technology into the automotive, aerospace, defense, and energy industries. In this study, the development process of additive manufacturing technology, which is constantly increasing worldwide interest, has been examined and evaluated within the scope of the literature.

2 History of AM

2.1 Start of 3D Printing

The simplest version of 3D prints, called Sterolithography (SLA), was first discovered by Charles "Chuck" Hull in 1980. Another element that triggered this development has been the development of laser technology. The SLA is a system where a light source of ultraviolet (UV) light focuses on the UV photo-curable polymer to harden it. It could be drawn several patterns using UV source to the semi-cured polymer pool. The semi-cured polymer remains in the bathroom, providing material support for the creation of the part produced. After a layer is completed during production, the hardened polymer moves down from the bath onto the building plate and forms the next layer that will be on top. This system is machining based on CAD design and continues until the production of the designed part is complete. In many cases, after the operation is completed, the part needs additional drying to be held by hand. Chuck Hull discovered this method in 1983 and founded 3D System companies that developed and produced 3D printers in 1986. This development can be expressed as the initial step in the emergence of the RP machine. And with this development, Chuck was the person who made it possible to create CAD files that were computerized by connecting them to the machine. This initiative was an important development for the development of 3D printers at the time. After developing this technology, Chuck Hull applied for a patent in August 1984, which was confirmed by the U.S. Patent and Trademark Office in 1986.

2.2 Development of Other RP Technologies

With this development, other inventors have started developing new AM machines that can use different materials and methods. Carl Deckard is a graduate student at the University of Texas at Austin and a professor at the same school. Joe Beaman started working on selective laser sintering, a new technology for that period. The SLS system works dependent on selective sintering of the production plate within certain areas of the production plate, forming the material to produce dust. When a layer of dust creates a layer of the part, the next layer of dust that follows creates another layer of dust, which continues until the part is finished producing. In this way, a 3-D-printed part is produced as a result of the accumulation of dust and sintering. Deckard and Beaman commenced constructing the machine in 1984 and discovered the first SLS device in 1986. Then they established Nova Automation, a company that later evolved into DTM Corp. In this way, they commercialized the SLS technology, making their first machines in 1989 called Mode A and Mode B. The company continued to manufacture SLS machines until it was purchased from 3D Systems in 2001.

Another AM technology was developed by Scott and his wife, Lisa Crump, who graduated from Washington State University. Scott, who had come out to make his daughter a toy, developed this technology by referring to the "molten deposit model". This technology consists of heating the thermoplastic to a semi-liquid state that will accumulate on the surface of the pad and reveal the layer. After Scott and Lisa developed this technology, Stratasys, Inc., started selling it by starting a forensic company. Stratasts, Inc. It has continued to grow from that day to today, and currently has several patented machines with a cost of between $2,000 and $600,000. Only some of the technologies listed above are being developed, and when 3D systems patented 3D printing technology, researchers from other parts of the world began to improve this technology. In 1988 and 1989, respectively, the NTT Data CMET and Sony/D-MEC firms in Japan began developing SLA systems. In Europe, companies like Quadrax and Electro Optical Systems (EOS) began to develop their 3D printing devices. This technology began to develop rapidly, with great interest worldwide [7].

2.3 From Rapid Production to Additive Manufacturing

Many technologies that have come to this stage are capable of making polymeric parts, but they are not capable of processing metal or ceramic materials. And these technologies were RP machines and were not appropriate for an AM in which finished items were obtained. A bit of development was needed for RP technology, which would also be used for metals and ceramics. Many companies were continuing their work on this issue. The first of these works was a Dr. from the EOS Company in 1989. Hans J. Langer and Dr. Hans Steinbichler were the pioneers in using SLA systems and, later, the SLA system to print plastic items. After that, they started to develop these studies to print metal parts in early 1990 and developed the first model of the direct metal laser sintering (DMLS) machine in 1994. They released the first DMLS system commercially in 1995. Operating in the same way as the SLS system, this system can only test for metal dust. This system contains numerous common engineering materials, including titanium alloys, aluminum, stainless steel, nickel, and cobalt. In 1997, EOS patented the existing line of products with laser sintering technology and sold it to 3D Systems. After this process, EOS has significantly improved SLS and DMLS systems, making EOS many successful and reactive AM firms in the world.

Another AM technologist developed the AM system in Sandia National Lab, located in Albuquerque, Mexico, that can produce metal components called “laser engineering and network shaping” (LENS®).This AM system was developed in 1997, and it was first sold by Optomec in 1998. The LENS® system works on the principle of the accumulation of metallic dust in a very strong laser latex, and the dust that melts solidifies on the previous lower plate. Optomec continued to develop LENS® and introduced to more than 150 customers since 2012. Another AM technique that is currently very popular was developed during the same period in which electron beam melting (EBM) is being developed. A company named Arcam AB developed this technology in 1997. EBM is based on the principle of teleporting an electron beam from a dust bed to selected areas. When a layer of dust is melted in the selected areas, it continues until the part is finished, which is the accumulation of another layer of dust on top of the previous one. Arcam AB, together with Chalmers University of Technology, first made it commercial and sold it to two customers in 2022. In 2007, the manufacturer of orthopedic implants produced a CE-approved Fixa Ti-Por hip implant using EBM technology. Since then, more implants have been produced by the EBM. Many critical items are able to be produced by EBM technology in the aerospace industry.

2.4 AM: Growing Technology

The AM industry is constantly growing, depending on all these developments. The curiosity about AM technology is so high that we can hear a new development every day. Many industries see the capability and cost benefits of AM and use AM technologies within them. In this way, the market is growing significantly. Many new RP and AM methods are used today, following the first applications and technologies mentioned above. This development has ensured the integration of many new features into the system and the diversity of materials that can be used. Starting as RP, LM, and SFF methodologies, these technologists have switched to AM technologies, where functional prototypes and parts can be produced to work in a variety of environments and conditions. In this way, AM's global market share has risen since the first 3D printers appeared. In 2012, the market share of 1850 million dollars reached 3475 million dollars in 2017. As technology and availability continue to increase, it is clear that this market share will increase further.

2.5 AM: New Manufacturing Paradigm

2.5.1 Current State of AM and How It Generally Works

AM technology has reached a ready point for industrial use today. It has advantages that create appeal in many industries compared to traditional methods. The most important advantage is that building layers by layer allows the production of parts with complex geometry. Although there are many different models and technologies, they all use the same principle and technique. First, a CAD model of the part to be manufactured is made, and this CAD model is converted to an STL file. Since Chuck Hill, the inventor of this business, the STL file has been a standard file for AM machines. The system then layers the model part to be manufactured. Then, various feeding and melting methods and materials to be used as raw materials are collected and connected in layers, and this process continues until the part is produced. In this way, the system enables the creation of incredibly complex geometries that are not able to be produced by other production methods. The manufacturing of complex geometric items needed in fields such as art, aerospace, and medicine can be done through AM technology.

2.5.2 Advantages of AM: No Limit on Design

It is estimated that AM technology will have a significant impact on many different industries, thanks to the ability to make components that were previously not possible through traditional manufacturing methods. The AM is able to produce the part with that complex geometry on its own, without the need for more than one operation. This capability of AM also gives designers great freedom. Because the design that is often needed can be complex and does not allow it to be produced by other manufacturing methods. There is no size limitation in the use of AM technology, but there are no restrictions that must fit in the machine. This uses only one machine, the AM machine. No additional processing costs are required. This results in a more cost-effective operation. The only cost other than raw material is the maintenance of the AM machine. No post-production processing is also required. Therefore, the addition of the material instead of processing is a manufacturing process, which also saves material. By reducing the manufacturing method, the milling process begins with a block that is larger than the product to be manufactured. Material is removed from the surface until the desired shape and dimensions are achieved, after which it is discarded or recycled. This creates additional costs. As there is no material loss in parts that are added to AM technology, up to 75% material savings can be achieved, and production costs can be reduced by 50%.

2.5.3 Advantages of AM: Versatility in Manufacturing

Another important and attractive aspect of AM is its versatility in production. It can be corrected by immediate intervention after detection of any defects in a manufactured part or design. AM technology can give manufacturers this opportunity. This can be difficult with other traditional manufacturing methods. For example, if you want to make a change to the design after an expensive mold is made in a casting process, you have to make another expensive mold. You may also not have a chance to quickly uncover the new mold. By using AM technology with significant production flexibility instead of long-lasting and expensive mold and/or part production, ready-to-use parts can be quickly produced at a lower cost. With this advantage of AM technology, it's easier for a designer to try new designs and to make the changes that a customer demands.

2.5.4 Advantages of AM: Altering Materials for Enhanced Performance

In AM technology, many engineering materials such as plastics, metals, composites, and ceramics are available. Depending on the part and technology that are intended to be completely produced, the material can be selected. Plastics are the most widely used, studied, and applied material in this material. Advances in AM technology are not only about the use of different materials but also about the development of hybrid production by creating new processes where different materials can be used. This is an example of the methods used by ceramics and metals to produce special abrasion-resistant composite parts. AM technology is also available for repairing critical parts and structures. In this respect, AM technology can be used not only for producing items with complex geometry but also for repairing damaged parts.

2.5.5 AM is in Modern Manufacturing

Today, AM is a standard manufacturing part for companies. The aviation industry has started using AM technologies to reduce the production cost of parts to be used in the engine. GE Aviation opened a facility with 60 EBM and direct laser sintering systems in December 2013. AM technology also allows for lighter engine parts to be produced. As a result, AM technology can optimize components, reduce weight, and minimize material loss. This brings an important financial advantage. Many other aeronautical companies, including GE, have begun to use AM.

2.5.6 Evolution of CAD to AM and Its Influence on Manufacturing

This incredible talent that AM technology provides has imposed a significant constraint on part design. One of the most important things that makes AM so attractive is that it allows a CAD file to produce a ready-to-use part. Thanks to developments in Chad, almost anything can be designed The CAD design converted into an STL file can be produced on an AM machine. This property gives engineers and designers the ability and flexibility to design more complex and efficient prototypes [34].

3 Additive Manufacturing Processes

Through the sequential addition of layers of material, AM enables the manufacture of models from three-dimensional computer-aided designs (CAD) [35]. The ISO/ASTM 52900:2021(E) standard categorizes AM processes into seven groups:

1. Binder jetting (BJ);
2. Directed energy deposition (DED);
3. Material extrusion (ME);
4. Material jetting (MJ);
5. Powder bed fusion (PBF);
6. Sheet lamination (SL); and
7. Vat photopolymerization (VP).

These categories are distinctive from one another in terms of how the layers are formed and how they are bonded to one another. *Binder jetting* is a method that selectively joins powder particles by depositing liquid binder droplets, allowing for the production of parts with near-net shapes [36]. The printed green parts frequently necessitate thermal post-processing, such as infiltration and sintering, to densify them and achieve the appropriate part properties [37]. This method can be used to manufacture large products and can work with a large materials range, including polymers, metals, ceramics, sands, and hybrid materials [38]. In the *Directed energy deposition* technique, a feedstock material (wire or powder) is fed to a substrate while an energy source is concurrently focused on it. This creates a small melt pool and provides for the layer-by-layer deposition of material [39]. DED systems are available in a variety of forms, for example: melt-based DED and kinetic energy-based DED according to the energy source; wire-feed and powder-feed-based DED according to the feedstock type. Melt-based DED can also be divided into subcategories such as electric arc, electron-beam, laser, and plasma-based [40]. Fully dense metallic pieces can be produced using the DED method for a variety of industrial applications [39]. *Material extrusion* is a method in which a feedstock is extruded and deposited in beads via a nozzle and substrate motion in relation to one another. The material is semi-solid throughout extrusion and solidifies once it is in its ultimate position and form [41]. The Fused Deposition Modeling (FDM) method is the most well-known ME technique [35]. The other techniques are Fused Layer Modeling (FLM) and Fused Filament Fabrication (FFF) [7]. ME techniques typically involve the use of viscoplastic materials like concrete, ceramic pastes, thermosets, and hydrogels [42]. Utilizing specialized nozzles, the *Material jetting* procedure deposits liquid material droplets across a building platform. This technology is sometimes referred to as Inkjet 3D Printing or Poly-jet Printing [35]. Typically, the droplets are made up of a mixture of the structural material and molten thermoplastic suspension or wax [43]. The newly formed layer is then typically solidified with UV light and transferred downward. Many times, multiple jetting heads are utilized, allowing for the simultaneous deposition of support material and other component materials. Support structures can be eliminated using a water jet or a chemical agent like sodium hydroxide solution [35]. Polymers, ceramics, composites, hybrid, and biological materials can be used in this method [7]. One of the earliest and still most adaptable AM techniques is *Powder bed fusion*, which works with metals, polymers, composites, and ceramics [44]. The PBF method operates under the fundamental tenet of layer-by-layer production and fusion of the product. The determined cross-sectional area of a powder-based material is heated by directing a heat source. As a heating tool, electron, laser, and infrared beam sources are utilized. The powder is able to assume the shape of the desired object by heating process. This method is extensively utilized in a variety of industrial fields, including the energy industry, aerospace, biomedical, and transportation [45]. The sub-categories of PBF techniques are Electron Beam Melting (EBM), Selective Laser Sintering (SLS), and Selective Laser Melting (SLM) [46]. To create quick, low-cost paper prototypes, *Sheet lamination* has been widely utilized. Then the utilization extended to polymers, metals, ceramics, and textiles, necessitating the development of procedures and equipment (3-D printers) [47]. According to ASTM, sheet lamination is a 3D printing process in which sheets of materials are bonded together to produce components of an object. Ultrasound Additive Manufacturing (UAM) and Laminated Object Manufacturing (LOM) are examples of 3D printing technology that utilize this procedure [48]. In *Vat photopolymerization*, liquid photocurable polymers that react to UV light undergo a chemical reaction and become solid [35]. VP techniques can be further divided into Stereolithography (SLA), Two-photon Polymerization (2PP), Volumetric 3D Printing, and Digital Light Processing (DLP) based on the variance in the curing source [49]. Polymer and ceramic materials can be used in this process [7].

4 Materials for AM

A variety of materials, including high-temperature alloys, shape memory alloys, high-entropy alloys, polymers, ceramics, biomaterials, composite materials, structural materials, hydrogels, biological tissues, food, and sand, are used in AM. AM uses powders, sheets, wires, inks, tissues, and other feedstock to build a net shape that is either fused or added together to manufacture a palpable 3D-designed product [50].

Metals and Alloys: AM of metals and alloys are mostly used in prototyping, investigation, and small-scale manufacturing in the aviation, aerospace, biomedical, automotive, and defense industries. Compared to traditional production techniques, AM of metals and alloys makes it easier to produce complex geometries [51]. Metal printing usually comprises PBF techniques that are activated with DED principles. Recently, additional metal printing methods such as BJ, Direct Metal Writing, Direct Metal Laser Sintering (DMLS), and Cold spraying have also been utilized to attain faster printing speeds and more precision [52]. Various metallic materials, including nickel-based alloys, titanium and its alloys, tool and stainless steels, sterling silver, aluminum alloys, brass, magnesium alloys, platinum, copper, bronze, and gold, among others, can be utilized in AM processes [51].

High entropy alloys: High entropy alloys (HEAs) have outstanding characteristics, including high temperature strength, good wear and corrosion resistance [53]. However, it is difficult to produce homogeneous alloys with the conventional casting method. AM may be a viable way for the fabrication of HEAs by facilitating process control, constituting fast solidification cooling rates, and enabling the fabrication of complex shapes [54].

Ceramics: AM is used in the production of 3D-printed ceramics and concrete without large pores or cracks. Ceramics are strong, durable, and fire-resistant materials. They are usable in the dental, construction, and aerospace fields. Examples of ceramic materials include bioactive glasses, zirconia, and alumina [55]. Ceramics are utilized in the AM process as powder, slurry, and bulk solid based feedstock [51]. In slurry-based methods, ceramic particles are dispersed in a semi-liquid system and used as feedstock in paste or ink form, depending on the system's viscosity. SLA, 2PP, DLP, Direct Ink Writing (DIW), and Inkjet Printing (IJP) are the technology kinds utilized to print slurry-based materials. Powder-based techniques utilize a powder bed format with loose ceramic particles as a feedstock. SLM, SLS, and Three-dimensional Printing (3DP) are the techniques utilized to print powder-based materials [56]. Sheets or filaments of the material are utilized as feedstock in bulk solid-based processes. In filament form, feeding is accomplished through deposition or extrusion. When using sheets as the feed material, the output is created by adhering the sheets together one at a time. LOM and FDM are technologies utilized in bulk solid-based 3D printing. In bulk solid-based ceramic AM materials such as lead zirconate titanate (PZT), glass–ceramic composite, Si-SiC composite, tape-cast Al_2O_3, ZrO_2 green sheets, and SiC are used [56].

Polymers: Due to their easy processing, lightweight, low cost, simple attainability, corrosion resistance properties, electrical and thermal properties and biocompatibility, polymers and polymeric composites are commonly utilized in AM [57]. SLA, SLS, FDM, LOM, 3D Bioprinting, 3D Plotting/Direct-Write, and Powder Bed and Inkjet Head 3D Printing are the most utilized polymer AM processes [56, 58]. Viscous polymer inks, photopolymers, polymer blends, thermoplastic filaments and powders, thermosets, hydrogels, elastomers, biological compounds, and polymer composites are the most widely used polymer materials for several AM processes. They have numerous implementations in different fields, such as automotive, biomedical engineering, soft robotics, aerospace, electronics, environment, and energy [55, 57]. Polymers, the majority of which are photopolymers, are the materials in the AM market that provide the most revenue. The photopolymerization method primarily utilizes the SLA technique. In this process, the molecular orientation of the printed item relies on the layer thickness, which is identified by the intensity of the UV radiation. Polyamides, thermoplastic elastomers, and polystyrene are typically utilized in SLS, the second most widely used technology. Liquid polymers, polymer filament, polymeric powders, and polymer films are the four types of polymer feedstocks most commonly utilized in AM processes. Photopolymers are utilized in the liquid state, thermoplastic polyurethane and Nylon 11 and 12 are utilized in the powder state, and a wide variety of thermoplastics are utilized in both the filament and powder states [55].

Composite Materials: By carefully choosing the fabrication process and the constituent materials, it is possible to regulate the mechanical properties and microstructure of composite materials. Free-form and multi-directional fabrication are both possible with AM. As a result, AM may be a useful production technique for multidirectional preforms made of composite materials [59]. AM applications of composite materials have long been researched in a range of industrial fields such as aerospace, medical, and architecture [55]. There are several applications for polymers and lightweight composites [59]. The two prominent examples are reinforced polymer composites with glass and carbon fiber [59, 60]. MMCs (metal matrix composites) are preferred over other traditional materials because of their superior mechanical characteristics. Research is being conducted on the production of complex 3D MMC parts with AM techniques. Mg, Al, Ti, Fe, Ag, and Ni are the widely utilized matrix materials, and the reinforcement materials are BC, graphite, Al_2O_3, SiC, BeO, Mo, TiC, NbC, TiB, W, TaC, and WC [52].

Smart Materials: Shape memory alloys (SMA), shape memory polymers (SMP), and smart nanocomposites like piezoelectric material are the main kinds of 3D printable smart materials. Also, there are certain multi-materials used to print actuators for soft robotics, anti-counterfeiting systems, and self-evolving structures. A highly effective way to print intelligent materials is with polyjet printing [56, 61].

Biomaterials: For use in organ transplantation and regenerative medicine, 3D-printed synthetic and natural biopolymers are being developed. Acrylate-based polymers, sodium alginate, and chitosan are examples of materials used. Furthermore, 3D functional living tissues can be generated. Dielectric elastomers, hydrogels, and shape-memory polymers are used to create biomedical equipment, artificial muscles, wearable gadgets, and other smart objects. Because of their processing challenges, such as high melting temperatures and complex phase formations, bioceramics are relatively new materials for AM. Bioceramics such as ceramic composites, bioglass, and calcium phosphates can be manufactured utilizing a variety of AM processes [62]. Metallic materials must be biocompatible in order to be used in the human body. Surgical-grade stainless steel, Ti and its alloys, and cobalt-chromium alloys are AM-machinable biocompatible metals [63].

Other Materials: Research on the use of AM technologies in the production of concrete and other building materials is increasing. With the development of textile printing, AM has found a place in the clothing and jewelry industries. In the food industry, food items can be produced through 3D printing using suitable food materials. Apart from these, studies on the use of AM technology in space exploration are ongoing. 3D printing of moon dust focuses on studies of colony infrastructures on the moon [55, 64].

5 Additive Manufacturing Technology General Workflow

AM technology has gained importance by virtue of the freedom of design it provides, the potential to produce complex shapes, and its time-saving features, unlike traditional manufacturing methods. Parts produced with AM generally have good mechanical properties such as low density, high strength, and high impact resistance [36]. In AM, feedstock materials, in powder or wire form, are selectively melted by a focused heat source to form a part and undergo simultaneous bonding and solidification processes. For some materials, including steel, aluminum, and titanium, it is possible to manufacture reliable and dense parts by the AM method with the developing technology. Most of the metal powders used in the AM process are generally produced using well-known technologies for metal powder production. These methods include water, gas, and plasma atomization. Generally, in the AM process, good flow properties are needed to ensure uniform spreading of the powder, and good packing properties are needed to form a high relative density powder layer. In addition, known as rapid prototyping and 3D printing, AM is a modern manufacturing method that enables devices with complex geometries. In the first step of the process, the part to be produced is modeled by means of computer-aided design programs (CAD/CAM). The 3D model is then sliced, converted to STL format, and printed. During printing, a layered structure is created by adding the next layer on top of each layer. After the process, finishing operations such as heat treatment and surface treatments can be applied, depending on the method and material used.

5.1 Industrial Application Areas of Additive Manufacturing Technology

The foundations of 3D printing, which is called an AM technique in the industry, were laid with the concept of Industry 4.0. Under the influence of the developing technology, a wide variety of AM examples are seen in the medical, aerospace, automotive, ordnance, architecture, personal equipment, fashion, education, and food sectors. The AM technique, which eliminates human resources in production, lowers costs and increases productivity by removing mold and prototype issues, which cause significant costs and time loss in the design process [65].

The first use of the AM technique in the industry was on prototypes developed for visual verification. For this reason, the AM technique is called "rapid prototyping" in the industry. AM is frequently preferred in the production of prototype parts, especially in the automotive industry. For example, after the Urbee vehicle was produced with a 3D printer, the final product parts used in the automotive industry were printed with this technique [66]. The need for a production line has been eliminated thanks to the use of 3D printers in the automotive industry. The AM technique alone can fulfill the task of many pieces of equipment that will occupy a large area. The reduction of production costs, the comparatively shorter manufacturing procedures, and the lighter weight of the created parts are some of the innovations that the AM method has provided to the aviation industry. The AM method has made it possible for nations without the necessary technology to make some parts for the aviation industry. The first professional use of AM in the construction industry started in 2007 with a 3D printer called D-shape [67]. The system, which can be used in the printing of building elements or the entire structure, works on the same principle as the laser sintering method (SLS). The use of structures produced with the 3D printing technique in war and disaster zones is among the future targets of the construction sector.

The AM technique, which allows the production of highly functional, professional, and customizable parts in the medical and dental sectors, enables the production of parts that are very difficult and costly to produce with traditional techniques at lower costs in a short time. Examples of AM use are dentures, orthoses, implants, dental products, surgical instruments, and the manufacture of tablets and capsules in the pharmaceutical industry. One of the most serious studies in the field of medicine is 3D bioprinting. In general, bioprinting is a technique used to produce living tissues. Materials such as hydrogel, silicone, and protein solutions are used in these printers. The main aim of the researchers who continue their studies in the field of bioprinting is to produce human organs with functional properties. 3D printing devices, which offer people the opportunity to learn through practice and develop their design-oriented thinking skills, are found in universities and schools. 3D printers play a very active role in academic studies and prototype development processes. The use of 3D AM technologies is also very popular in the food industry. AM enables the production of healthy products with rich nutritional values. Considering these situations, the use of AM in the food industry is becoming more common day by day. In the fashion sector, AM has a large share of the global market. The AM process, which is comparatively popular in the fashion industry, is gradually increasing its market share. Because the sector consumes a lot of natural resources, 3D printing provides a relatively easy way to reduce this.

6 Recent Developments in Additive Manufacturing Technology

Biomedical Application

One of the main disadvantages of AM technologies is that their manufacturing capacity is limited. While this limitation could be a disadvantage for many industries, in medicine or healthcare, patient-specific devices or implant designs do not need mass production. Hence, AM is progressively used in many applications in healthcare as new biomaterials are developed [68]. Tappa et al. [69] and Pradeep et al. [70] reviewed the biomaterials used for additive manufacturing. Deposition technology heavily depends on the materials that need to be adjusted to the place where implants or prosthetics are placed. The fused deposition or free-form fabrication method is the most common method of AM technology. A thermoplastic filament is passed through a heated plate and scuffed on the support plate layer by layer until the model structure forms. The most common materials used in the FDM process are polylactic acid (PLA), polyamide, polycarbonate, and polyvinyl alcohol. PLA is a well-known biocompatible polymer with a melting temperature of around 175 °C, thus making it easy to load drugs. AM has tremendous advantages in biomedical applications. Patient-specific production and prototyping could be applied by using a scanner and modeling the following device to be developed by any technology. For example, spinal cages used to replace spinal disks are made from PEEK [71, 72], which needs relatively high melting temperatures compared to other polymeric materials. A cranial implant, which is a highly patient-specific implant used to treat face-related problems, is successfully manufactured via additive manufacturing [73]. Polymeric-based materials and metallic-based materials are used to replace some of the organs, primarily bone tissues. Metallic materials often exceed bone tissue elastic modulus, resulting in a stress-shielding effect and aseptic loosening [74]. Titanium cages have internal pores that make their elastic modulus similar to that of natural bone, and the pore radius and percentage can be controlled using AM technology. Pores also play a different role as a placeholder filled with drugs or agents to heal bones that could be easily produced by additive manufacturing technologies, especially laser melting or electron beam melting technologies. Zhang et al. [75] have reported that titanium cages produced by electron beam melting and filled with simvastatin hydrogel promote bone ingrowth and spinal fusion in rhesus macaques. Another comparative study [76] revealed that additively manufactured titanium cages outperformed conventional PEEK cages without using a bone graft. AM technology is not limited to engineering biomaterials; even living cells could produce various materials with varying viscosities, and high cell density aggregates can be 3D printed. The first “bioprinted living tissue implant” went to a 20-year-old woman born with a small, misshapen ear [77, 78]. This technology involves obtaining chondrocyte cells from patient-impacted ear following cells mixed with bio-ink and 3d printed by a protective biodegradable material. The implanted ear matures with time and develops the characteristics of a native ear. Additive manufacturing for biomedical applications requires innovative biomaterials with specific characteristics of biocompatibility and formability. Efforts are being made to improve multi-functional biomaterials and bio-inks for this purpose.

Aerospace Applications

Metal additive manufacturing (MAM) is a crucial type of AM used in the aerospace industry due to the need for complex parts that cannot be easily made using conventional methods. This technology allows for metals and metal alloys that cannot be used in traditional manufacturing methods. The earliest application of AM in aerospace applications was for product prototyping and tooling. However, nowadays, AM is effectively used to produce complex-shaped parts.

In the past decade, research into metal additive manufacturing (MAM) has focused on developing various alloys to suit qualified aerospace/gas turbine applications. Alloys such as AlSi10Mg, Al7Si0.5Mg (F357), AlMgSc, Ti6Al4V, γ-TiAl, CoCrMo, Stellite12, IN718, IN625, CM247LC, HastelloyX, SS316L, CuCrNb, and CuCrZr fall into this category. The aim is to create materials with isotropic microstructures and high defect tolerance that can be adopted in the aerospace industry. The development of difficult-to-weld chemistries, alloys prone to cracking, and alloys with improved high temperatures are also being researched [79].

Ceramic materials, known as high-temperature, corrosion, wear and abrasion resistant, efforts are being made to develop ceramic materials in additive manufacturing technologies. SLM can achieve some solid-state or liquid-phase sintering of ceramics, but during the process, excessive thermal differences often result in crack formation that limits the usage of ceramics [80]. Lakhtar et al. [81] summarized their findings after reviewing Engineering Ceramic and several applications using AM methods. As MAM and alloy development significantly impact aerospace applications, another aspect of additive manufacturing technology is emerging. While SLM, EBM, and DED methods are well-known applications for manufacturing metal-based products, the high melting temperature of ceramic materials limits the usage of those methods. Ultra-high temperature materials (>3000 °C) such as HfC and ZrC are used in rocket combustion chambers, thrusters, and solar energy applications [82, 83]. Processing refractory ceramics into complex geometries is challenging, even with advanced ceramic processing techniques.

A recent application [84] that provided a first material in powder form and a second material as a consumable electrode successfully produced several ceramic-based materials using additive manufacturing methodology. In this process, applying electrical energy to initiate a chemical reaction between the materials helps form a reaction product. This process, named “reactive additive manufacturing,” showed that a variety of materials, such as TiC, TiB_2, B_4C, SiC_2, $Al_2O_3 + {}_3TiC$, could be manufactured layer by layer. Given a showcased example, an exothermically reactive mixture containing 76% aluminum and 16% titanium and boron carbide powders produced a product with an aluminum matrix and TiB_2 and TiC-reinforced composite under argon-purged vacuum conditions using a direct metal laser sintering (DMLS) machine, available from EOS of North America, Inc. of Novi, MI (US). It is now obvious that metal additive manufacturing is anticipated to have a significant long-term influence on the aerospace sector, opening the way for the next generation of product design based on the recent success stories of industrial adoption and implementation.

7 Conclusion

Industrial interest in additive manufacturing (AM) technology is growing day by day. Significant technological gains have been achieved by using different production techniques and by using a single process to manufacture complex or high-precision parts that are specifically determined in the industrial area to which they are applied. The use of AM technology has extended to a wide variety of industries, from the aerospace industry to the biomedical industry, owing to the advantages of the process, including originality in design, use of advanced technologies and materials, precise tolerances and complex geometries in production, long-lasting use, and low material consumption. In the future, advances in AM technology will make it possible to repair damaged materials and material groups as well as produce a variety of precision parts that are widely utilized in critical sectors. This study examines and presents AM technology, industrial application areas, and the most recent developments in the process based on several industries.

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Chapter 2
Challenges in Additive Manufacturing Technology: Post Processing, Design and Material's Selection

Hamaid Mahmood Khan and Saad Waqar

Abstract It is important to bear in mind that additive manufacturing (AM) did not emerge in isolation but rather built upon earlier technologies. The rapid adoption of 3D printing technology across industries serves as a testament to its effective evolution from a specialized method primarily used for prototyping to a viable industrial production technique. As the trend continues to gain momentum, an increasing number of companies will inevitably embrace AM techniques to manufacture components using diverse materials. This chapter explores significant milestones in the history of additive manufacturing, illustrating the advancements 3D printing has made over the past decade while considering the widespread growth of applications and technology in the mainstream. The transformative journey of 3D printing is examined, shedding light on its profound impact on various industries and its potential for further development and innovation in the future. By examining the historical context and current landscape, this chapter aims to provide a comprehensive understanding of the progressive nature of additive manufacturing and its continued role in shaping the manufacturing industry. In Sect. 1, a brief introduction is given regarding the historical and future trends in additive manufacturing. Sections 2–6 discuss different additive manufacturing techniques, their working principles, and the suitable materials for each of these techniques. In Sect. 7, the concept of 4D printing is briefly discussed, including its applicability and future trends.

Keywords 3D printing · Additive manufacturing · Stereolithography · Photopolymerization · Powder bed fusion

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1 Introduction

Over the past few decades, the use of 3D printing techniques has significantly expanded across various industries. This expansion has resulted in increased productivity and the development of cost-effective and sustainable methods of fabrication. In particular, numerous biomedical and aerospace companies have already begun utilizing 3D printing operations to create intricate metal parts that are lightweight [1, 2]. Instead of the earlier research-focused 3D printers, several prominent manufacturers of 3D printing machines are now optimizing their devices to cater to industrial applications and large-scale production. Figure 1 depicts some well-known manufacturers of 3D printing machines, many of which have experienced commercial growth in the last ten years.

Currently, the majority of commercially available additive manufacturing (AM) systems are designed for producing polymeric materials, which make up approximately 72% of the market. However, despite their large market share, the commonly used polymeric materials like polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) are not suitable for high-end applications due to their limited resistance to extreme environmental conditions. In order to meet the demands of such applications , there is an increasing focus on exploring other materials with high resistance to extreme conditions, such as carbon-reinforced composites, polycarbonate, polyether ester ketone, polyetherimide, and nylon. These materials are being investigated for their potential applications and fabrication using AM techniques [3].

Fig. 1 Main 3D printing vendors in the market

Furthermore, polymer-based 3D printers are expanding their manufacturing capabilities beyond prototypes and models to functional parts, including tooling, spares, and end-use components. Similarly, the composite 3D printing industry offers significant opportunities for fabricating lightweight and high-strength components. 3D-printed parts with continuous fiber reinforcement can be exceptionally lightweight while maintaining strength comparable to metal. Additionally, discontinuous fiber-based composite materials like metal matrix composites find extensive applications in the medical and aerospace industries [4].

While the ceramic 3D printing industry is not currently prominent, it is expected to experience significant growth in the coming decade. Advanced ceramic materials such as alumina and zirconia exhibit exceptional mechanical strength, temperature resistance, and chemical resistance, making them viable options for the aerospace and electronics sectors. The application and fabrication of these materials with exceptional properties using AM techniques will greatly increase the utilization of AM printers across various industries.

The following section will provide a detailed discussion on various 3D printing techniques, their working principles, and their application areas in terms of materials and industries. This will help to enhance understanding of the future of additive manufacturing (AM).

2 Vat Photopolymerization

In Vat Photopolymerization, the process involves the use of ultraviolet (UV) radiation or other light sources to cure or solidify photo-curable resins [5, 6]. Different light sources are used depending on the specific application and requirements. UV radiation and electron beams are commonly used light sources for photopolymers in general applications. UV light has a shorter wavelength and higher energy, making it effective in initiating the polymerization process and achieving fast curing times. Electron beams, on the other hand, can provide precise control over the curing process and are often used in industrial settings.

In the case of dental products, visible light is predominantly used as the light source. Visible light has a longer wavelength compared to UV light and is less harmful to the human body. Dental photopolymer resins are formulated to be sensitive to visible light, allowing for safe and efficient curing during dental procedures [7]. The choice of light source depends on factors such as the desired curing speed, material properties, safety considerations, and specific application requirements. UV and electron beams are more versatile and commonly used in various industries, while visible light is preferred in dental applications for its safety and compatibility with dental materials.

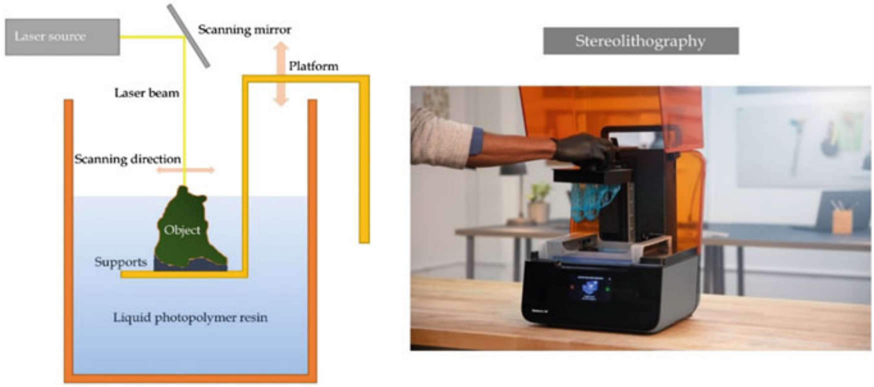


Fig. 2 SLA process description and SLA 3D printer (*Source* FormLab)

Stereolithography (SLA) is one of the most popular photopolymerization technique to fabricate solid 3D geometries from a pre-defined CAD model. Figure 2 shows the schematic diagram of the SLA process and the desktop model of the SLA 3D printer. Digital light processing (DLP) technique is another Photopolymerization technique that utilizes a digital light projector for the curing of polymers. The advantage of DLP technique is that a single layer can be processed at once, thus increasing the productivity of the whole process [5, 8]. Given the earliest versions of photopolymerization technique, the maturity and popularity of SLA is well developed than other photopolymerization processes. Given the extensive research in SLA technology, considerable progress in structural features, like dimensional accuracy, surface quality, ease of fabrication of complex models, material waste reduction, and rapid process automation, has been achieved successfully. However, the necessity for a support structure, the instability of cured resin, the high cost of machines, and the need for ongoing maintenance are some of SLA challenges that requires more attention [9].

Photopolymer resign materials have been deeply researched and tested in different techniques to produce models for various industrial applications. Standard or structural resins account for most of the photopolymer material in SLA techniques, attaining high accuracy, high rigidity, and low creep under high temperature conditions. Resins like polypropylene (PP), polyethylene (PE), ABS, and elastomeric polyurethane (EPU) are commonly adopted materials for SLA and other Photopolymerization techniques. Interestingly, by using suspended power in the photo polymers, metal and ceramic components are also reported to be manufactured with SLA and other light based 3D printers [6, 10, 11] (see Table 1).

Table 1 Outlining the process parameters and their effects in vat photopolymerization

Process parameter	Effect
Resin type	Different resins have varying mechanical properties, such as flexibility or rigidity, and can affect the final object's strength and durability
Photo-initiator concentration	The concentration of the photo-initiator affects the curing time and the depth of cure, which determines how deep the layers can be solidified
Exposure time	Longer exposure times result in more complete curing, leading to stronger parts but may increase printing time. Shorter exposure times may result in insufficient curing and weaker parts
Layer thickness	Thinner layers allow for higher resolution but increase the total number of layers and thus printing time. Thicker layers reduce printing time but may sacrifice surface quality and detail
Light source power	Higher light source power can reduce curing time but may also increase the risk of overheating or warping the object. Lower power can result in longer curing times
Scanning speed	Faster scanning speeds reduce the printing time but may sacrifice accuracy and resolution. Slower speeds enhance detail but increase the total printing time
Build platform temperature	Temperature can affect the resin's viscosity, curing speed, and shrinkage. Different resins have specific temperature requirements for optimal performance
Supports	Supports are used to stabilize overhanging structures during printing. Their placement and design affect the surface quality and the need for post-processing
Cleaning and post-processing	Proper cleaning and post-processing steps, such as rinsing with solvents or UV curing, can affect the final surface finish and mechanical properties of the printed object

3 Material Extrusion

Extrusion-based 3D printers have gained a significant market share due to their simplified processing method. These printers work by pushing a semisolid material (known as extrudate) from a reservoir through a nozzle, depositing it layer by layer onto a platform to create a solid structure. One crucial aspect of the extrusion process is ensuring that the extruding material flows at a consistent and uniform rate. This is necessary for proper layer consolidation, ensuring that each newly extruded layer bonds well with the preceding layer. The material can be supplied to the reservoir in either discrete, separate unit (such as pellets or filaments) or in a continuous form (such as a granular feedstock) [12].

The extrusion process is depicted in Fig. 3, which showcases a schematic model of the Material Extrusion (MEX) process. This process is widely used in various applications and industries, including prototyping, product development, and even in some production-grade applications. It offers advantages such as relatively low cost, compatibility with a wide range of materials, and the ability to create objects of different sizes and complexities. By leveraging the extrusion-based 3D printing

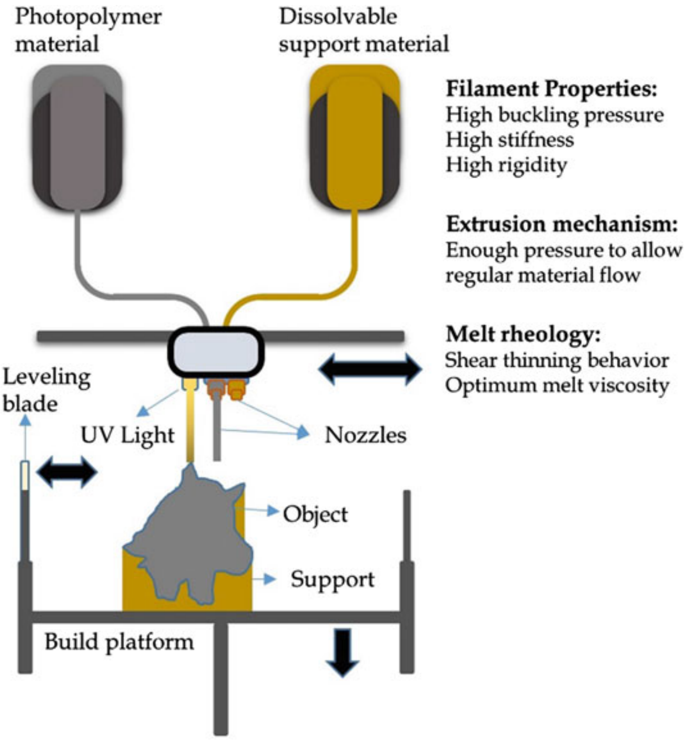


Fig. 3 Schematic model of Material Extrusion system

method, manufacturers and creators can produce solid structures by depositing layers of extrudate, enabling them to bring their designs to life.

In the Material Extrusion (MEX) system, there are two widely used approaches for achieving material bonding. The first approach involves regulating the temperature of the extruding material, while the second approach involves adding chemical agents such as curing agents (UV-sensitive and heat-activated curing agents) or residual solvents (acetone). In the temperature regulation method, it is important to provide sufficient input energy to activate bonding. Insufficient energy may result in cracks between layers, while excessive energy can cause the extrudate to flow, leading to reduced component accuracy.

Controlling the flow rate and pattern of the extruded material in the MEX system relies on critical parameters such as pressure drop, nozzle shape, and material viscosity. Using a larger nozzle allows for extruding more material, but at the expense of accuracy. On the other hand, smaller nozzles can provide better accuracy and minimum feature size but increase build times significantly [3]. Moreover, compared to line-wise or layer-wise scanning techniques, the point-wise plotting technique used in MEX systems requires frequent changes in direction, making the operation slower. Low-cost MEX machines with simple designs are capable of processing a range of materials to produce parts with acceptable mechanical properties. Some commonly processed materials in MEX machines include PLA, ABS, ASA, a PC-ABS blend, and TPU.

4 Binder Jetting

Binder jetting technology (BJT) is another prominent AM technique which utilizes an array of parallel nozzles for quick patterning and colored component manufacturing. In the BJT system, a liquid from the nozzle droplet applied to a layer of powder bed is used to bind the powder particles inside powder layer together as well as with the previously printed layer. Following the layer printing, the printed layer is lowered by one-layer depth to allow for the deposition of fresh layer of powder particles through the recoating procedure. Similar procedure is repeated multiple times unless the complete part has been fabricated. At the end of the process, parts are left in the powder bed for a long period to set the binder or reinforce the green part [13]. However despite the simple nature of the process, BJT components are often require post-processing operations like sintering or hot isostatic pressing, to achieve desired mechanical properties and to fuse the powder particles together for longer component life [14]. Figure 4 shows the line diagram of the BJT system. Table 2 presents a concise overview of the history and progress of Binder Jetting technology:

For component fabrication, BJT can process a broad range of materials, such as plaster-based powder or a water-based binder. Some machines also have a color print head to create aesthetically appealing components. In terms of metals, BJT can

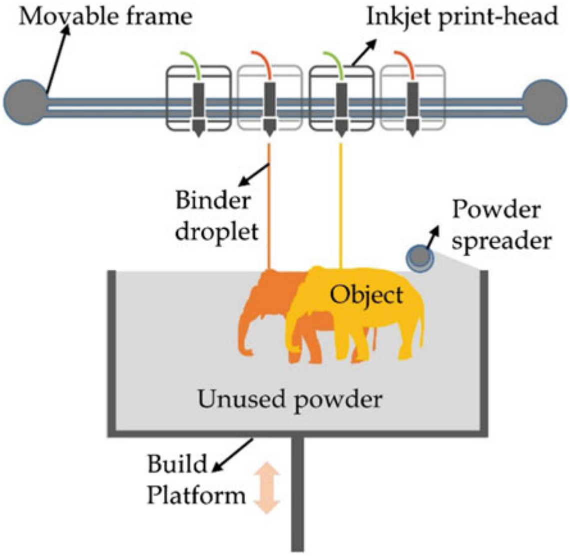


Fig. 4 Schematic model of Binder Jetting system

Table 2 Outlining the brief history and progress of Binder Jetting technology

Year	Milestone
1988	Conceptualization of Binder Jetting technology by researchers at the Massachusetts Institute of Technology (MIT)
1990	Development of the first prototype Binder Jetting machine at MIT
1996	Formation of Z Corporation (now 3D Systems) and introduction of the first commercially available Binder Jetting 3D printer, the Z402
Early 2000s	Advancements in Binder Jetting technology, including improvements in print speed, resolution, and material options. Introduction of color printing capabilities
2010	ExOne introduces the M-Flex, an industrial Binder Jetting system, expanding the technology's capabilities for large-scale production
2015	HP enters the Binder Jetting market with the introduction of the HP Jet Fusion 3D Printing Solution, targeting both prototyping and production applications
2017	Desktop Metal unveils the Studio System, a Binder Jetting system designed for office-friendly metal 3D printing
Present	Continued advancements in Binder Jetting technology, with improvements in print speed, accuracy, material options, and integration with post-processing techniques. Growing adoption in industries such as automotive, aerospace, and healthcare

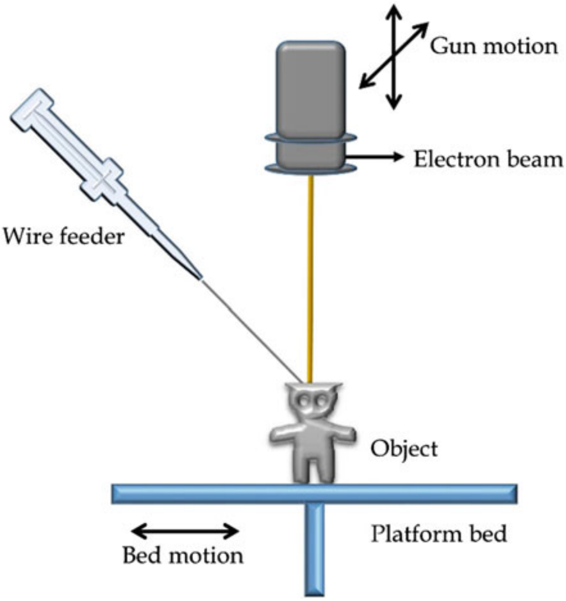
handle a wide range of stainless steel alloys, including 316L, 17-4PH, 304L, and 420 steels, and ceramics, like alumina, silica, and titanium dioxide [15]. Binders are typically removed from metals via heating, although in some situations, low-melting point metals can be utilized to infill pores to boost component strength [16]. Other metals, such as Inconel, tool steels, cobalt chrome, and tungsten alloys, are also now being tested in the BJT method. Multiple heat-treatment cycles can be performed to achieve the desired strength in fabricated parts through furnace heating [17].

5 Direct Energy Deposition

Directed Energy Deposition (DED) methods are highly advanced and commercially successful additive manufacturing (AM) processes. These methods involve depositing molten metal onto a heated platform or previously deposited layers to create solid components. The metal deposition process is guided by the relative motion of the substrate and the deposition head, which can include laser optics, powder nozzles, and inert gas tubing. Both powder and wire can serve as feedstock in DED machines, but laser deposition of metal powder is the most commercially viable approach [18, 19]. Figure 5 illustrates the key components of a basic DED model.

Powder feeding mechanisms in DED systems can employ co-axial feeding, 4-nozzle feeding, or single nozzle feeding. Co-axial feeding utilizes an integrated nozzle to deliver the laser beam, powder particle stream, and shielding gas. The powder stream surrounds the laser beam, while the shielding gas directs the powder

Fig. 5 Schematic diagram of directed energy deposition method



stream towards the melt pool, providing protection against oxidation. Co-axial feeding allows for increased introduction of powder particles into the melt pool. Single nozzle feeding, on the other hand, employs a separate nozzle for powder and the laser beam. This approach offers cost-effectiveness, simplicity, and improved powder capture compared to the 4-nozzle feeding system. The 4-nozzle feeding system features four separate nozzle heads evenly spaced at 90 degrees, facilitating the fabrication of complex 3D structures with varying thicknesses.

While DED machines predominantly utilize 3-axis systems, 4- or 5-axis systems incorporating rotary tables, robotic arms, or DED machines integrated with multi-tool CNC milling systems are being developed to enable multi-functionality. Wire feeding systems in DED have minimal material loss, making them ideal for fabricating simple geometries or coating surfaces. However, achieving pore-free and dimensionally accurate structures in a single pass is challenging with wire feeding technology. As a result, DED systems are typically adjusted to produce dense components, with integrated milling systems used to add dimensional precision [20, 21].

DED machines can be categorized further based on the heat source, including laser, friction stir, electron beam, and arc-powered DED devices. Some modern DED machines incorporate electron beam sources and wire feeders [22].

Laser cladding is a similar process used to join similar or dissimilar metals using roll bonding, explosive welding, or laser bonding processes. Laser cladding offers improved tribological behavior and resistance to liquid or gas flow, high-impact situations, wear, and abrasion resistance [23, 24]. Dense layer deposition and high layer thickness in 3D laser cladding enable faster build rates and longer component life with reduced maintenance and part replacement. Laser cladding is often employed for repairing large-scale metal components. Electron beam DED machines are commonly used in space applications due to their high deposition speeds, vacuum processability, efficient energy consumption, and rapid operation [25]. Wire feeders are well-suited for low-gravity environments, offering ease of manufacturing, effective material handling, and reduced material waste.

Friction Stir Additive Manufacturing (FSAM) is a process similar to DED that utilizes friction stir welding technology in an open-air environment. FSAM enables alloying, component repair, metal joining, and other applications by boosting the temperature of metal feedstock through plastic deformation, facilitating layer fusion via solid-state bonding. FSAM can process non-weldable materials with significantly lower residual stresses and thermally-induced porosity [26]. The key aspects of the DED process is given in Table 3.

Table 3 Summarizing the key aspects of Directed Energy Deposition (DED)

Aspect	Description	Effect
Process parameters	*Parameters that affect the DED process*	
Laser Power	The power of the laser beam used for melting the material. Higher power results in faster melting and deposition	Higher power can increase material melting and deposition rates, but excessive power may cause overheating and distortion
Powder/Wire Feed Rate	The rate at which the powder or wire feedstock is delivered to the deposition zone. Controls the deposition rate and material build-up	Higher feed rates result in faster material deposition, but excessive rates may lead to incomplete melting and poor bonding
Scanning Speed	The speed at which the laser or deposition head moves across the workpiece. Affects the layer thickness and overall printing time	Faster scanning speeds reduce overall printing time, but slower speeds can improve accuracy and surface finish
Layer Thickness	The thickness of each deposited layer. Determines the resolution and strength of the printed part	Thinner layers provide higher resolution, while thicker layers decrease printing time but may sacrifice detail
Powder Flow Rate	The rate at which powdered material is delivered to the deposition zone. Controls the material distribution and density	Proper flow rate ensures uniform deposition, while inconsistent flow can lead to irregularities in material distribution
Atmosphere Control	The control of the gas environment in the deposition chamber to prevent oxidation or other undesirable reactions	Maintaining a controlled atmosphere prevents oxidation and improves material properties
Materials used	*Commonly used materials in DED*	

(continued)

Table 3 (continued)

Aspect	Description	Effect
Metals	Stainless steel, titanium, aluminum, nickel alloys, etc.	
Alloys	Tool steel, bronze, copper-nickel, Inconel, etc.	
Ceramics	Alumina, zirconia, silicon carbide, etc.	
Composites	Metal matrix composites, ceramic matrix composites, etc.	
Famous brands	*Prominent brands offering DED systems*	
DMG Mori	Offers LASERTEC systems for DED	
Trumpf	Provides TruLaser Cell systems for DED	
SLM Solutions	Known for its Selective Laser Melting (SLM) technology, which is a form of DED	
Sciaky	Offers Electron Beam Additive Manufacturing (EBAM) systems, a variant of DED	
Optomec	Specializes in Aerosol Jet systems for DED	

6 Powder Bed Fusion

Powder Bed Fusion (PBF) remains one of the most commercially successful and widely applied AM processes, being well-suited for polymers and metals and, to a lesser extent, ceramics and composites [27]. The Selective laser sintering (SLS) method, which was originally designed to create polymeric prototypes, was one of the first commercialized PBF techniques. Later, after modification to the working principle of SLS, selective laser melting (SLM), direct metal laser sintering (DMLS), and electron beam melting (EBM) processes came into existence. A numerically controlled heat source is used in the PBF system to fuse discrete powder particles dispersed in a micron level thin layer to recreate a 2D contour of a 3D CAD model [27, 28]. Although PBF techniques are more suitable for metallic materials, yet with certain limitations they can be considered for other materials as well. While thermoset polymers are unsuitable for the PBF system due to their high-temperature degradability, thermoplastics are easily curable. Polyamide (nylon), notably polyamide 11 and 12, are the most commonly used thermoplastic polymer for the PBF system [29, 30].

Selective laser Melting (SLM): In SLM machines, powder particles heating is achieved by absorbing a photon from a laser beam. As a result, the temperature of a powder rises above its melting point, forming a liquid melt pool that solidifies to

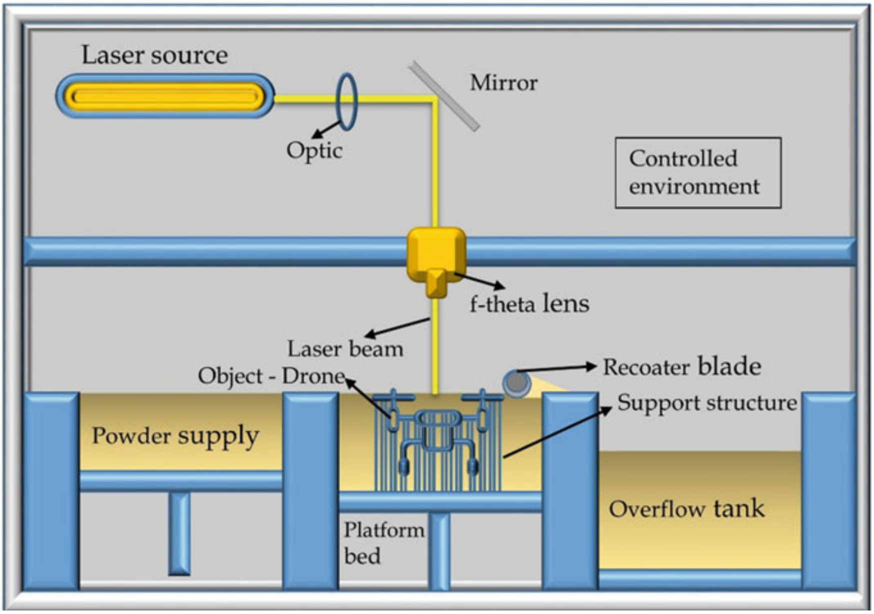


Fig. 6 Schematic representation of SLM system

form a solid structure after returning to the ambient temperature. In the SLM process, the laser source melts the powder region as well as some layers beneath it completely, allowing for strong consolidation between layers [31]. Beside creating dense components, SLM is also well suited to manufacture complex 3D components, such as nature-inspired lattice materials and topologically optimized lightweight fuel- and cost-efficient structures. Auxetic metamaterials, cellular lattice structures like TPMS, or strut-based designs can provide applications having high energy as well as shock absorptivity, and high heat dissipation [32]. Figure 6 shows the schematic model of the SLM system.

As of now, SLM can process several alloys, such as Al, Ti, Ni, Co–Cr, stainless steels, high entropy alloys, and more. Any weldable metal is considered to be a good candidate for the SLM system. Along with metallic materials, Ceramic materials are also widely investigated using the SLM technology. Metal oxides (aluminum oxide and titanium oxide), carbides, nitrides, and their mixtures can be used in a variety of applications [33]. Biocompatible materials with ceramics are now frequently used in bio-industries. In comparison to polymers, metal processing in AM systems is rather challenging due to the metals' high thermal conductivity, laser reflectivity, oxidation, and high surface tension. The parts during solidification can exhibit 3–4% shrinkage, which can lead to part distortion. Thus, materials with low thermal conductivity can provide better accuracy as melt pool and solidification will be more controllable due to the limited part growth [2, 34]. Regardless of the material type, optimizing process parameters is essential to obtain desired microstructural and mechanical features for SLM components. Although interdependent, these process parameters can be categorized into four types [28]:

i. Laser parameters—power, spot size, pulse duration, pulse frequency, etc.
ii. Scanning parameters—scan speed, scan spacing, scanning patterns, etc.
iii. Powder parameters—powder material, size, shape, distribution, and packing density, layer thickness, etc.
iv. Temperature-related parameters—powder-bed and powder-feeder temperatures, temperature uniformity, etc.

Electron beam melting (EBM): Powder heating in an electron beam powder bed fusion process, which is also known as EBM, is achieved by the transfer of kinetic energy from incoming electrons. In contrast to lasers that can process any laser absorbing materials (metals, ceramics, or polymers), electron beam source is suitable for only conductive materials like metals. Moreover, electron beam source is cost-effective and highly efficient, which is not the case with the laser beam. In case of lasers, only 10–20% of the total electrical energy is converted into beam energy, with the remaining energy lost in the form of heat. However, fiber lasers are cost effective, as they are capable of providing conversion efficiencies of about 70–80%. EBM, on the other hand, can provide approximately 100% conversion efficiency. Depending on the feedstock material and heat source parameters, SLM/EBM process can be optimized to attain desired densification and structural accuracy [35]. Another advantage of EBM machines over SLM machines is that due to the considerably high penetration depth of electron beam, the layer thickness in EBM can be quite large, thus resulting in high productivity of EBM. Large components are therefore often preferred to be produced with EBM. Platform bed in the EBM system are maintained at high temperatures for better charge connectivity. This results in the induction of high incident energy from the electron beam source, causing the microstructure of EBM parts to be significantly different from the SLM part. As a result, the grain size in EBM parts are coarser like cast microstructure, and melt pools are wider than the SLM part. Moreover, residual stress in EBM part is lower than the SLM part due to the elevated bed temperature. Like the SLM system, support structures are also necessary for the EBM process for part stability and electrical conductivity. However, support volume in EBM can be significantly lighter, making their removal much easier. This enables the EBM system to have a clear advantage when it comes to minimizing residual stress and supports [36].

7 4D Printing

While 3D printing is often compared to assembly line production, its slow speed and limited volume capabilities hinder its widespread use for mass production. Additionally, 3D printing is limited in terms of its applicability to only a fraction of available resources. However, 4D printing, an extension of 3D printing that incorporates time as the fourth dimension, addresses these limitations by significantly reducing manufacturing time, typically by 70 to 90%. The materials used in 4D printing, such as programmable shape memory alloys, polymers, metal alloys, and ceramics, possess self-sensing, self-repairing, self-assembling, and multifunctional properties when exposed to environmental factors like temperature, humidity, magnetic fields, pH, water, air, and light [37].

Compared to 3D printing, 4D printing enables the rapid development of intelligent, flexible, and deformable structures with multiple materials, offering potential for novel applications [38]. Five essential components are required for successful 4D printing: a reliable 3D printing process, responsive smart materials and their unique stimuli, interaction mechanisms, and mathematical modeling. Mathematical models describe the material's behavior and duration during shape changes, while the interaction mechanism, such as mechanical loading, determines the desired shape change in response to a stimulus [39].

4D printing finds broad applications, particularly in the biomedical field, including orthodontics, endodontics, prosthodontics, oral surgery, and implantology. Although not yet commercialized, 4D printed dental implants have the ability to mimic natural teeth by undergoing shape changes in response to variations in oral temperature and humidity [40]. Similarly, in space applications, low-cost materials capable of withstanding extreme conditions are highly desirable. The compact storage space on spaceships makes 4D printing an excellent solution for creating self-adapting components that can change shape and size upon deployment. The potential for repairing satellite components without relying on supplies from Earth has been demonstrated through 3D printing using ABS and Nitinol (a nickel and titanium shape memory alloy) in space. Additionally, the production of low-cost, lightweight smart sensors using 4D printing holds promise for providing intelligence to vehicles, drones, and other objects. The use of intelligent, self-healing materials could be a significant advancement in manufacturing, as these materials can be repeatedly utilized, resulting in reduced material consumption [41].

While 4D printing holds great potential, there are several restrictions and challenges that need to be addressed before it can be widely adopted. Currently, 4D printing is primarily limited to research institutes due to the constraints in available materials, designs, and technology. Technological advancements are necessary to develop new printing methods that can enable the 4D printing of a broader range of smart materials. Additionally, the modification of existing additive manufacturing (AM) techniques or the development of new sustainable techniques is a complex task, as only a few AM technologies are capable of printing smart materials in 4D.

Another limitation of 4D printing is the potential for undesired characteristics to manifest over time. For instance, polymer materials may experience degradation from repeated wetting and drying, while metal structures like nickel-titanium (NiTi) can undergo continuous deformation. These challenges call for the development of more robust materials and improved durability in order to ensure the long-term performance of 4D printed objects.

Furthermore, 4D printing currently faces limitations in achieving high resolution when printing complex structures. To overcome this, the concept of 5D printing has emerged. By incorporating nozzle and printing bed rotation, 5D printing enables multi-axis object printing, facilitating the rapid and precise fabrication of curved surfaces. Notably, 5D printed objects utilize less material and exhibit increased stiffness compared to 4D and 3D printing techniques [42, 43]. Addressing these challenges and advancing the technologies associated with 4D printing and its extension to 5D printing will pave the way for wider adoption and unlock further opportunities in the field.

8 Conclusion and Future Work

Industrial and large-scale manufacturing processes are undergoing significant transformation with the emergence of new industrial alliances, substantial investments, and rapid advancements in materials and technology. Modern 3D printers have the capability to produce components that are larger than the printers themselves, making them highly versatile for various industries including aerospace, defense, automotive, healthcare, food, electronics, and more [44].

Over the past decade, 3D printing has gained increasing attention from governments, educational institutions, and businesses, leading to its growing popularity. According to a report by Mordor Intelligence, the 3D printing market, which was valued at $13.7 billion in 2020, is projected to reach $63.46 billion by 2026, with a compound annual growth rate of approximately 30%. 3D printing enables the rapid, efficient, and cost-effective production of customized parts. The advancements in modeling and slicing software have made the 3D printing process easily accessible, allowing seamless interaction between computer-aided design (CAD) models and 3D printers.

In contrast to conventional manufacturing techniques that require expensive tools and dies, 3D printing offers greater flexibility in managing small inventories, reviving outdated designs, constructing intricate lattice structures, and repairing or manufacturing damaged goods. This limitless potential of additive manufacturing (AM) has been a driving force behind numerous innovations. Designers now have unparalleled freedom for prototyping, design iterations, and product personalization. Furthermore, the development of new materials has expanded the possibilities of 3D printing, with a wide range of options including thermoplastics, composite filaments, photosensitive resins, metal alloys, and ceramic materials. Selecting the appropriate material for a specific product's physical and chemical requirements has become much easier with 3D printing technologies.

The impact of 3D printing extends to various fields. For example, affordable, lightweight, and electrically powered prostheses can be 3D printed, allowing amputees to regain full control of their arm movement. Patient-specific surgical models, antimicrobial dental implants, dentures, and impression trays can all be easily created using various 3D printing technologies. Additionally, topological optimization techniques enable the production of lightweight aviation components, reproduction of obsolete parts for classic cars, and customization of automotive seats, resulting in 3D printed parts with improved structural integrity and fuel efficiency.

In traditional industries, complex molds created using 3D printing technology significantly reduce fabrication costs and labor-intensive production steps, enabling faster and cost-effective production of components in large quantities. Combining conventional manufacturing methods with AM can help address significant production challenges. On-site process monitoring instruments allow for real-time adjustment of component quality by modifying process parameters, environment conditions, and temperature without the need to stop the machine mid-operation. AI-driven generative designs further enhance the capabilities of 3D printing by reducing the number of iterations required to achieve optimal designs. Generative design engines provide a range of organic shapes that fulfill specific design requirements based on given constraints such as dimensions, materials, manufacturing processes, and service loading conditions. These capabilities empower 3D printing to revolutionize the way items are manufactured. Overall, 3D printing is driving transformative changes in the manufacturing landscape, enabling the creation of new designs and products that were previously unimaginable.

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Chapter 3
Nano-structured Materials in Additive Manufacturing: Synthesis, Properties, and Applications

Anshuman Patra

Abstract Nano-structured materials have extensive applications in electronics, defence, automotive, aerospace, space. Some of the distinct properties of nanomaterials such as excellent strength, ductility, wear resistance encourages the application in structural domain. Additive manufacturing, also interpreted as 3D printing is a cost-effective fabrication route through layer-by-layer deposition of metal. The method can produce the final product with little or no machining requirement, and the process can be tailored to achieve the bulk product with desired properties. Several nanomaterials synthesis routes used in additive manufacturing processes, major advantages and challenges of introduction of nanomaterials, properties of fabricated component and applications will be discussed in the chapter.

Keywords Nanostructured materials · Additive manufacturing · Synthesis techniques · Properties · Applications

1 Introduction

Nanomaterials possess a dimension of less than 100 nm and exhibit exciting properties compared to micron size materials. With increasing demand of cost effective, near net shape products with desired final properties for structural applications, several synthesis routes of nanomaterials such as mechanical alloying, sol–gel technique, chemical and physical vapor deposition, temperature-assisted decomposition, laser ablation etc. have been developed [1]. The nanomaterials are further consolidated to produce the final product. The properties of the nanomaterials need to be retained in the consolidated product with the objective of sustainable applications. In the present

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time researchers have fabricated complex products comprising nanostructured materials for cutting-edge applications. The requirement of microstructure, properties, and complexity varies based on applications. Therefore, additive manufacturing (AM) has evolved as an exciting fabrication technique. The final product quality depends on the initial powder characteristics such as powder size, shape, flowability. Strondl et al. have studied the impact of different AM methods, such as selective laser melting (SLM) and electron beam melting (EBM), on powder characteristics [2]. The study reports that recycled powder (powder exterior of consolidation zone) exhibits improved flowability due to the presence of less fine particles compared to the powder subjected to consolidation by SLM [2]. It is also indicated in the literature that oxygen content and porosity significantly impact the mechanical properties of the component fabricated from SLM [2]. A variety of products such as sensors, robotic arm, heat insulation, flexible electronics are fabricated by AM, and addition of nanomaterial adds further progress to advancement [3–5]. Nanomaterials addition during 3D printing process can be done at the beginning or at the intermediate stage [6]. Though homogenous nanoparticles can be achieved, however agglomeration of nanoparticles still needs to be addressed for property enhancement [6, 7]. The book chapter includes a review of the involvement of nanomaterials in additive manufacturing processes. Different fabrication routes, and interesting properties of nanomaterials for improved AM product quality are also discussed.

2 Categories of Nanomaterials

Nanomaterials can be classified based on dimensions such as zero-dimensional (0D), one dimensional (1D), two dimensional (2D), and three dimensional (3 D). The 0D nanomaterials such as quantum dots facilitates stability during AM, sensitive to sensor and therefore used for biosensors, optoelectronics etc. [8]. The 1D nanomaterials (perovskite nanowires, carbon nanotube) also offer exciting optical, electrical, and magnetic properties [8, 9]. 2D nanomaterials are sheet based with thickness less than 5 nm [10], possess extensive surface area, and chemical, physical properties are anisotropic [11]. Graphene as 2D nanomaterial has become the focus of research due to its outstanding electrical, thermal and mechanical properties [12]. Due to several exceptional properties, the 2D nanomaterials find applications in energy storage [13] , batteries [14], biomedicine [15], catalysis [16] etc. 3D nanomaterials include nanoballs, nanopillers, ordered nanowires arrays [17–19]. Literature reports that 3D carbon nanomaterials can be used for solar energy conversion by combining graphene (2D) and carbon nanotube (CNT) (vertical, 1D) [19]. The 3D nanostructure possesses a high surface area which is effective for more charge accumulation and is therefore used in supercapacitors [20] and as a catalyst in fuel cell [21]. The nanomaterials comprised of crystallites can exhibit similar or variations in composition among the crystallites, different compositions between crystallites and interfacial area, and dispersed crystallites in matrix with varied composition [22].

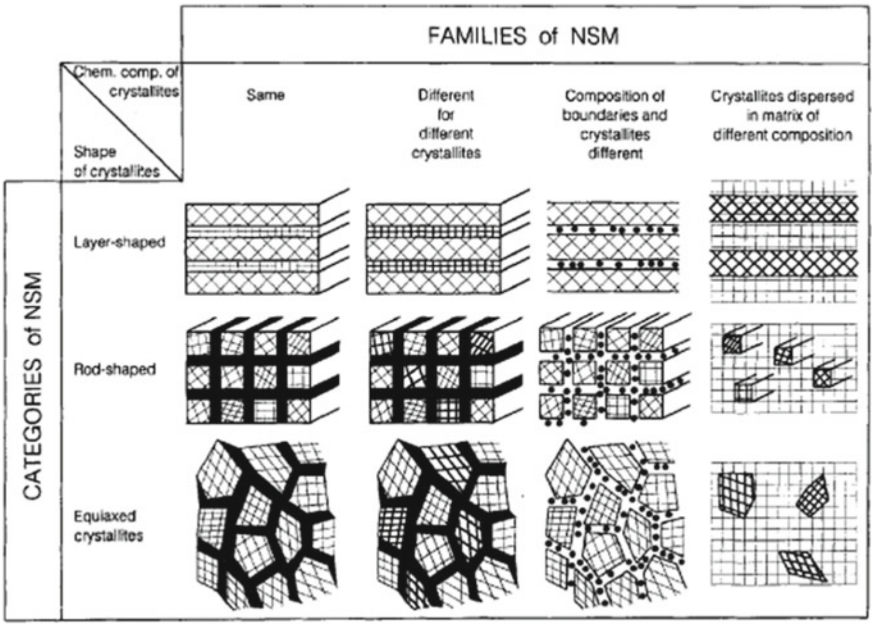

Fig. 1 Categories of nanostructured materials based on shape and chemical composition, Reprinted from Nanostructured Materials. **6**, Gleiter, H., Nanostructured materials: state of the art and perspectives, pp. 3–14. Copyright (1995), with permission from Elsevier [22]

The nanomaterials can be of several types based on their final dimension and shape, as presented in Fig. 1.

Nanomaterials can contain different metals such as Ag, Au and finds application in medical industry due to significant biocompatibility [23–25]. The nanomaterials in metal oxides form can be used as below:

Fe_2O_3: therapeutic [25], CeO_2: antiinflamation [26], TiO_2: drug delivery, bone regeneration, vascular stents [23, 24, 27], ZnO: drug delivery, bioimaging, biosensing [28, 29]. Additionally ceramic centred nanomaterials for tissue engineering [30] and polymer-based nanomaterials for bone-fixing device, dental applications are also important [31].

2.1 Nanomaterials for Additive Manufacturing

The synthesis can be divided into several categories according to the literature evidence [22] such as:

(a) Physical vapor deposition, chemical vapor deposition, atmospheric interaction with oxygen.

(b) Extensive deformation (mechanical alloying/milling, shear extrusion, irradiation driven).
(c) Rapid solidification.

The properties of the nanomaterials can be enhanced by functionalization techniques. Molecules such as surfactants, polymers, inorganic constituents can be combined on the surface of nanoparticles by physisorption, chemisorption, electrostatic interaction [32, 33]. The involvement of functionalized nanomaterials in AM technique can facilitates cost-effective devices for medical industry [34]. For AM process, the final size can be either in millimeter or in microns (20–50 µm) [35, 36]. Recent trend in electronic, automotive, medical industries is to reduce the size [37], and therefore the development of AM methods with nanoscale size limit is essential. However, the AM technologies have to be judiciously selected to achieve minuscule product. The nano-size product by AM has commercial significance, such as 3D microbattery electrodes [38], microrobots for medical industry [39]. Other literatures also indicates the use of nano thermites in ammunition, pyrotechnics [40] due to significant surface area (around 10–50 m^2/g), reduced temperature and time of ignition, elevated energy density (50 MJ/kg) and rate of burning [41, 42]. The safety related to the synthesis and transport of thermites due to hazardous nature imposes challenges. The addition of several nanoparticles (Fe, Ag) in the sintered parts produced by 3D printing shows significant value addition related to reduced shrinkage and shape deformation [43, 44]. The reported challenges of integrating namomaterials with AM are as following [45]:

(a) Cost of nanomaterials
(b) Stability in environmental conditions
(c) Agglomeration.

Therefore, it is necessary to use functional nanomaterials for AM use. The nanoparticles can be separated by using organic molecules. Lao et al. have reported that suitable nanoparticle distribution can be achieved by adding carbon nanofibers to laser-sintered powders using screw extrusion method [46].

3 Synthesis Techniques

3.1 Screw Extrusion

Several methods are used to mix nanomaterials with the matrix. Mixing of nanomaterials with polymer matrix is possible by screw extrusion (single/twin). In the screw extrusion process as presented in Fig. 2, viscous materials is added through the inlet [47] and pressure effect restrict the backward movement of the injected material [48]. Screw having lowest thickness should possess adequate strength for enduring shear and friction forces. Literature evidences that extrusion rate and temperature need to be precisely regulated to improve the product quality [48]. The 3D printer is attached

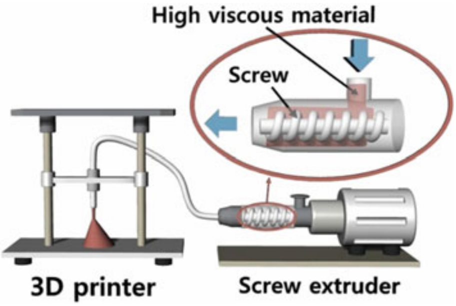

Fig. 2 Schematic of Screw type extrusion with 3D printer, Reprinted from Ceram. Int. **45**, Kim, N. P., Cho, D., Zielewski, M., Optimization of 3D printing parameters of Screw Type Extrusion (STE) for ceramics using the Taguchi method, pp. 2351–2360. Copyright (2019), with permission from Elsevier [47]

to the screw extruder to hold the deposition for developing 3D products [49]. The velocity of deposition is controlled by adjusting the speed of rotation of the screw [49].

3.2 Sol–Gel

Sol–gel has been reported as potential preparation method of nanocomposites. The major advantages of sol–gel method are [50]:

(a) The method can be carried out at usual temperature, pressure.
(b) Chemical constituents can be regulated effortlessly.

The schematic representation of sol–gel technique is provided in Fig. 3 [51]. The objective of these methods is uniform dispersion of nanoparticles in polymer. Nanoparticles as colloidal suspension are subjected to evaporation for removing the solvent and finally solidification followed by different consolidations to achieve bulk products [52]. Kumar et al. have prepared Tb and Li co-doped ZnO nanoparticles by sol–gel method [25]. Silica nanoparticles are dispersed in polyurethane by sol–gel method and improvement in biocompatibility which illustrates the application of the nanocomposites in biomedical sector [52].

3.3 Electrospinning

Electrospinning technique is utilized for the production of nanofibers. The method is found to be of great interest in tissue engineering applications. In this technique, electrostatic forces are applied to a polymer solution to stretch it in the form of fibers. The high voltage is used in the process causes jet formation of the polymer solution

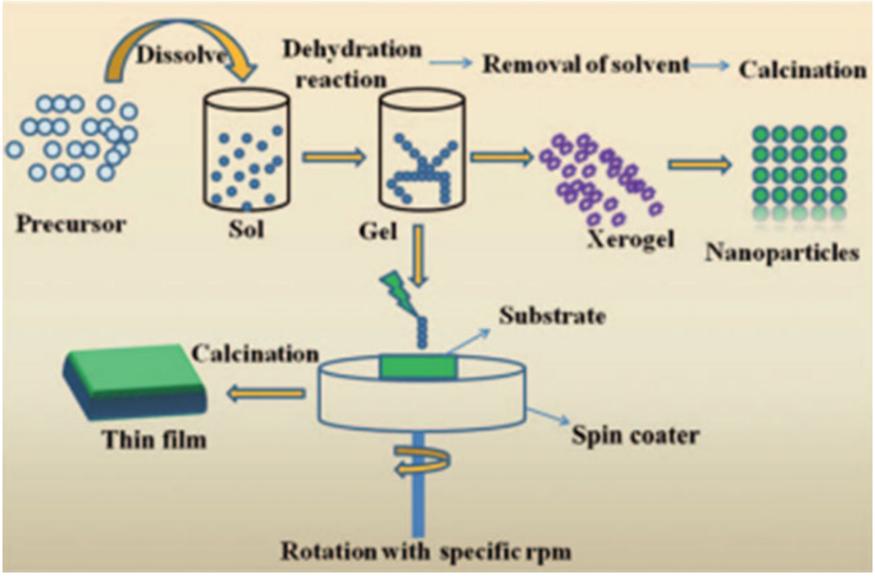

Fig. 3 Schematic of sol–gel method, Reprinted from Micro and Nano Technologies, Additive Manufacturing with Functionalized Nanomaterials. Kumar, P., Kumar, R., Synthesis process of functionalized ZnO nanostructure for additive manufacturing: a state-of-the-art review. Singh, S., Hussain, C. M. (eds.), pp. 135–153. Copyright (2021), with permission from Elsevier [51]

drop followed by evaporation of solvent and production of fibers in the collector zone as described in Fig. 4. Several factors, such as applied voltage, solution flow rate, distance between tip and collector, viscosity of solution impact the fiber development process [53]. Polyvinyl alcohol/collagen with nano-hydroxyapatite [54], fibrous scaffolds from elastomers [55] have been prepared by electrospinning method.

3.4 Coprecipitation

Material's synthesis through coprecipitation technique produces homogeneous composition with reduced size. In this method aqueous salts are combined with a suitable basic constituent and during precipitation phase oxalates/hydroxides nucleate in the solution [56, 57]. The solution is further heated to achieve the required product. The coprecipitation has the following major advantages [58, 59]:

(a) Increased output
(b) Reproduction is effortless
(c) Cost-effective synthesis.

However, there are certain disadvantages of the process such as [60–64]:

(a) Precipitation of impurities

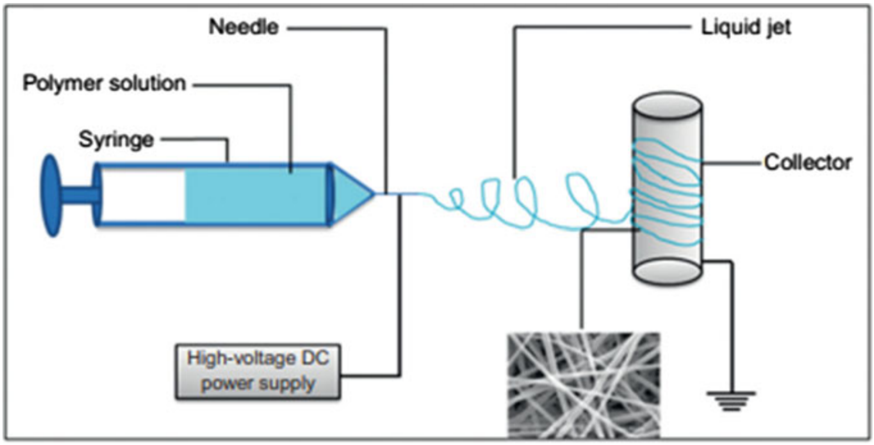

Fig. 4 Schematic of Electrospinning set-up, Reprinted from Nanotechnology Applications for Tissue Engineering, Unnithan, A. R., Arathyram, R.S., Kim, C. S., Electrospinning of Polymers for Tissue Engineering. Thomas, S., Grohens, Y., Ninan, N., (eds.), pp. 45–55. Copyright (2015), with permission from Elsevier [53]

(b) To control the final purity several treatments of the nanoparticles are required.
(c) Generation of hazardous waste material.

Figure 5 shows the steps for the production of NiO nanoparticles using Ni (II) nitrate hexahydrate precursor [63]. Literature suggests that the morphology of the nanoparticles can be controlled by the application of surfactants, sonochemical techniques, reactive precipitation using high gravity. Several researches have been performed to obtain nanomaterials through coprecipitation such as $NiFe_2O_4$ (particle size: 28 nm) [65], ZnO nanoparticles (140 nm) [66], $CoFe_2O_4$ (particle size: 19 nm) [67], Fe_3O_4 (15 nm) [68].

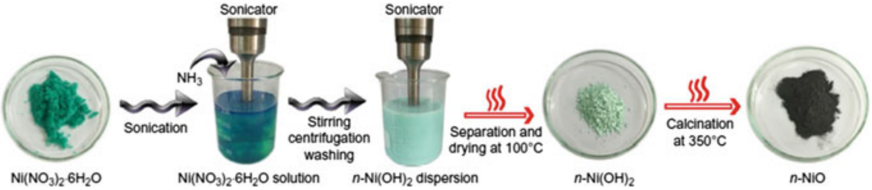

Fig. 5 Preparation method of NiO nanoparticles by co-precipitation method, Reprinted from Micro and Nano Technologies, Synthesis of Inorganic Nanomaterials. Ashik, U. P. M., Kudo, S., Hayashi, J., An Overview of Metal Oxide Nanostructures. Bhagyaraj, S. M., Oluwafemi, O. S., Kalarikkal, N., Thomas S., (eds.), Woodhead Publishing, pp. 19–57. Copyright (2018), with permission from Elsevier [63]

3.5 Mechanical Alloying

Mechanical alloying includes the reduction of particle size and formation of solid solution, amorphous alloys, intermetallic phases through deformation of powders [69]. In the process vial containing grinding balls, with or without process control agent, elemental powder(s) is rotated at a certain speed and time to achieve the required size, degree of alloying. However, the required size depends on several parameters such as ball to powder weight ratio, diameter of grinding ball, temperature of milling [69]. Contamination from vial, grinding ball can also generate during milling. Therefore, the application of process controls agents, milling in inert atmosphere, and judicious selection of grinding ball can be options to minimize the contamination [69]. Solid-state deformation, mixing of elements with poor solubility in each other, cost effectiveness, product homogeneity are the significant benefits of the process [69]. Mechanical alloying is effective for synthesis of alloy containing constituents with wide variations in melting temperature, specific weight and vapor pressure. Alloy such as Ta–Ti is therefore difficult to process through melting-casting route due to poor homogeneity and mechanical properties [70]. Khimich et al. have reported the synthesis of Ti–Nb alloys by mechanical alloying followed by laser powder bed fusion and indicate non cytotoxic nature and appreciable porosity required for biomedical applications [71]. It is also indicated that mechanical alloying is a successful synthesis method of nanomaterials as a substitute for spheroidization process [71]. Literature shows that a number of steps in traditional processing (Mechanical alloying + consolidation) involve additional post-processing of the final product [72]. Combining mechanical alloying and AM route reduces the processing steps as presented in Fig. 6.

3.6 Electric Explosion of Wires

In this technique, a metallic wire is subjected to significant pulse of electric current for production of nanoparticles. The method utilizes elevated current density (10^{11}–10^{12} A/m^2), short time duration (10^{-8}–10^{-5} s) resulting in melting, evaporation and plasma formation [74–76]. Nanoparticles are formed from the condensation of atoms in aqueous, gaseous, or organic medium [77–79]. Various metals [80], oxides [81], nitrides [82], carbides [83], alloys [84] can be synthesized by the process. Electrical explosion of W wire in liquid paraffin for production of metastable WC powder is displayed in Fig. 7 [83]. Process parameters such as wire mass, gas pressure, applied energy regulate the final particle size [85]. Sato et al. have reported that the particle size of palladium is smaller when pulsed wire discharge is carried out in Ar medium compared to N_2, He due to less necessary energy for ionization in the process [85]. Tanaka et al. have indicated that a higher diameter of wire produces fine particles due to higher vapor content and rate of nucleation, and the particles are of spherical shape at all studied wire diameter [83, 86].

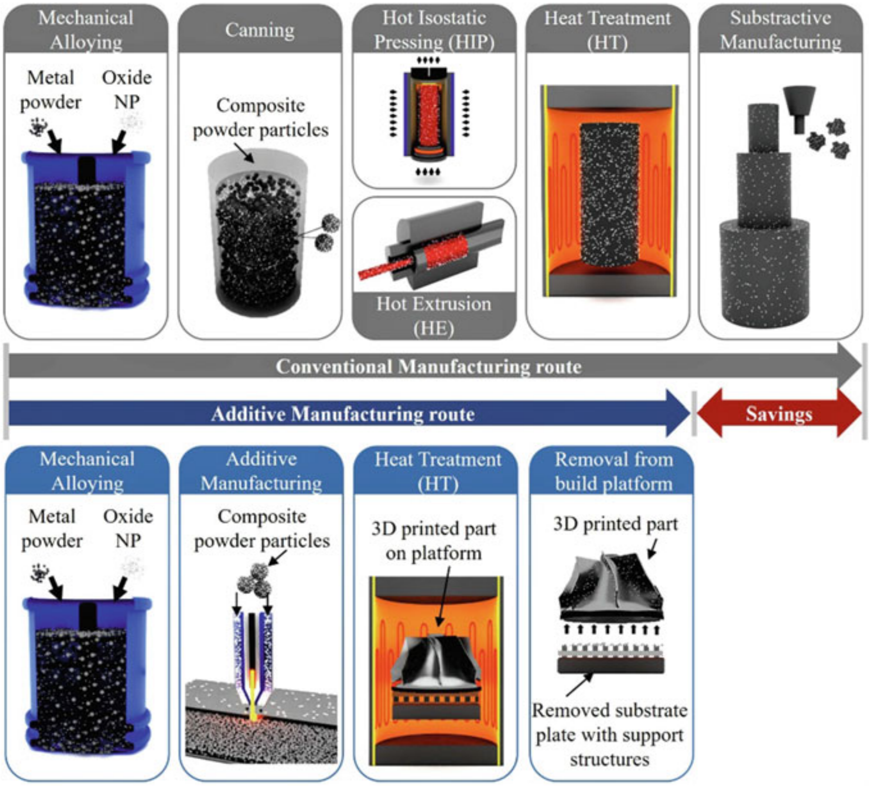

Fig. 6 Comparison of conventional processing [73] with additive manufacturing processing route of ODS alloys, Reprinted from Prog. Mater. Sci., **133**, Wilms, M. B., Rittinghaus, S. K., Goßling, M., Gökce, B., Additive manufacturing of oxide-dispersion strengthened alloys: Materials, synthesis and manufacturing. 101049. Copyright (2022), with permission from Elsevier [72]

4 Effect of Nanomaterial During Additive Manufacturing

Products fabricated by additive manufacturing show enhanced properties with the addition of nanoparticles. Lin et al. reported that dispersing 35 vol.% TiC in Al matrix considerably refines the grains (331 ± 95 nm) from 2.7 ± 1.4 μm (in pure Al) [84] by fabrication through Laser additive manufacturing. The process improves the laser absorption capacity, substantial yield strength (till 1000 MPa), and thermal stability (till 400 °C) [87]. The mechanism of melting of nanoparticles during melt-assisted additive manufacturing can provide comprehensive idea about the advantages and challenges of using nanomaterials. The surface roughness associated with laser metal additive manufacturing is counteracted by addition of nanoparticles. Qu et al. have indicated significant improvement of viscosity in 4.4 vol.% TiC nanoparticle added Al6061 compared to Al6061 alloy [88]. The paper also reports that complete damping of surface waves has been achieved by nanoparticle addition in Al6061 alloy resulting

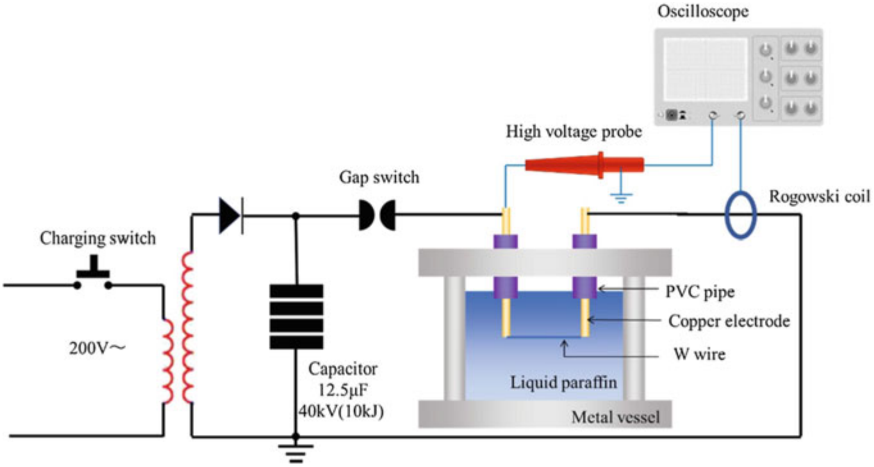

Fig. 7 Schematic of electric explosion of wire technique, Reprinted from Adv. Powder Technol., **29**, Tanaka, S., Bataev, I., Oda, H., Hokamoto, K., Synthesis of metastable cubic tungsten carbides by electrical explosion of tungsten wire in liquid paraffin, pp. 2447–2455. Copyright (2018), with permission from Elsevier [83]

in enhanced surface quality [88]. It is also reported that addition of Al_2O_3 nanoparticles in Ni reduces the heat transfer, heat-affected zone, and increases the melting zone as presented in Fig. 8 [89].

The effect of nanoparticles addition on melting and solidification behavior is reported in several literatures [90–92]. The TiN nanoparticle rearrangement is contributed by the developed Marangoni flow in the AlSi10Mg–TiN composite melt

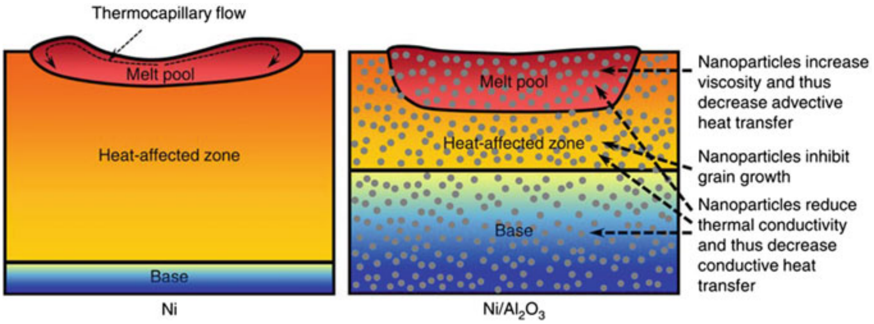

Fig. 8 Schematic of melting and solidification by laser melting of pure Ni and Ni with Al_2O_3 nanoparticles addition, Reprinted from Nat. Commun., **8**, Ma, C., Chen, L., Cao, C., Li, X., Nanoparticle-induced unusual melting and solidification behaviours of metals. 14178. Copyright (2017), with permission from Springer Nature [89]

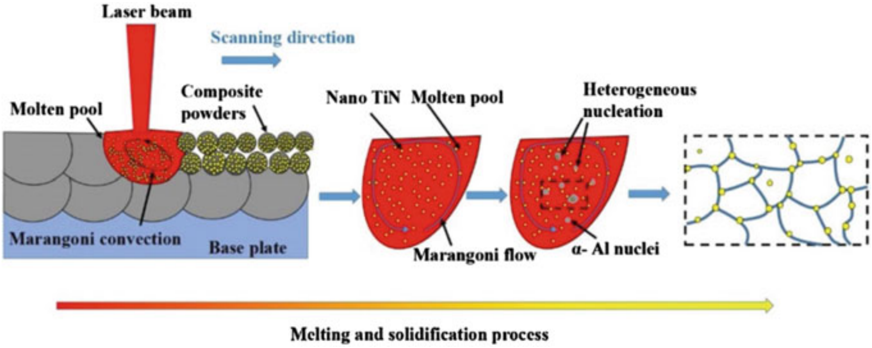

Fig. 9 Schematic of the progression of melting and solidification in AlSi10Mg–TiN composites fabricated by SLM technique, Reprinted from Addit. Manuf. **34**, Gao, C., Wu, W., Shi, J., Xiao, Z., Akbarzadeh, A.H., Simultaneous enhancement of strength, ductility, and hardness of TiN/AlSi10Mg nanocomposites via selective laser melting. 101378, Copyright (2020) with permission from Elsevier [90]

(Fig. 9) [90]. The nano particles provide heterogeneous nucleating spots and therefore, grain refinement can be achieved. Intergranular TiN nanoparticles are highly populated (control the grain growth) compared to intragranular regions [90].

The concentration of nanoparticle addition is also crucial to restrict agglomeration during melting. To minimize the agglomeration effect of nanoparticles, one of the strategies is the engineering of the surface with some surface modifiers. Literature suggests that the application of acetylacetone hinders the agglomeration of aluminium nanoparticles [40]. During the synthesis of powder for additive manufacturing, by introducing solvent and polymer the stirring speed and time need to be accurately controlled to minimize agglomeration. In another study, friction stir additive manufacturing has been used to control the nanoparticle accumulation, and homogeneous distribution by re-stirring and reheating phenomenon evolved during the process [93]. Kaldre et al. have successfully disperse SiC nanoparticles inside the grain of Al–Mg alloy, however agglomeration is reported in Sn sample even through the application of acoustic cavitation introduced by electromagnetic method [94]. Dispersion of Y_2O_3 and $Y_3Fe_5O_{12}$ nanoparticles has also been obtained by pulsed laser irradiation technique [95]. In laser power bed fusion (LPBF) method, the major focus is to enhance the efficiency of laser power. Report indicates that TiC nanoparticles addition in Al6061 alloy fabricated by LPBF enriches the mean energy efficiency by 114% owing to vapor depression [96]. The major reasons for such enhancement of energy efficiency related with material's properties are: (a) increase in absorptivity, (b) reduction in thermal conductivity [97]. One of the key methods to improve product quality in additive manufacturing is electropulsing treatment (EPT). The methods include several advantages, as listed below:

(a) Homogenization of microstructure [97, 98].
(b) Decrease in residual stress [99]
(c) Formation of equiaxed grains [100].

Additionally, EPT has been applied for improvement of superelasticity with a controlled time period [101], and enhancement of mechanical properties in NiTi shape memory alloy compared to conventional heat treatment methods [102]. It is also reported that the dissolution temperature of Ti_3Ni_4 in the matrix is less (around 300 °C) by application of EPT compared to traditional annealing (in excess of 600 °C) [103]. Moreover, the current applied in EPT process needs to be controlled to achieve finer precipitate size and enrichment in mechanical properties [103].

As discussed in the preceding sections, the addition of nanoparticles improves the properties of products fabricated by AM. However, the characterization of required properties depends on final application area. Using nanoparticles (ZnO) in biomedical field requires careful attention as higher concentration (500 mg/kg) (such can also result in variation in blood parameters and negatively influence several body parts [28, 104]. Literature shows that the addition of 4 wt.% TiN nanoparticles in AlSi10Mg is adequate to attain enriched densification (porosity: 0.01%), hardness (156.9 ± 4.9 HV), ultimate tensile strength (491.8 ± 5.5 MPa), ductility (7.5% ± 0.29) of the composite fabricated by selected laser melting [90]. Tan et al. have reported that the addition of Ti nanoparticles in 2024 aluminium alloy contributes to the following attributes [92]:

(a) Improvement in mechanical properties in both transverse and longitudinal direction.
(b) Remove the anisotropy in properties.
(c) Enhancement in resistance against hot tearing.

The effect of nano SiC addition in AlSi7Mg alloy developed by SLM is displayed in nanoindentation study (Fig. 10a, b). It is evident that 2 wt.% nano SiC addition reduces the average displacement of the indentation, which supports reduction in deformation [91]. Corresponding improvement in average Young's modulus and nanohardness is presented in Fig. 10b [91]. To achieve the required properties, and dimensional tolerance few attributes at different stages of processing are of significant importance. The stages and the corresponding attributes are as following [105]:

(i) Feedstock (solid, liquid): Surface composition, surface energy (corresponding to wettability), texture (related with anisotropy), roughness.
(ii) Component fabrication: Dimension of component, droplet size, grain size, defects, extent of heat dispersal, dispersion.
(iii) Post processing: Internal stress, grain size, defects, roughness.

The wettability of ink on the substrate in inkjet printing needs to be considered for uninterrupted distribution. Therefore, the contact angle between ink and substrate has to be less than equals to 90°. Additionally, the surface tension of the ink should be lower than the substrate [106]. High particle wettability is beneficial to enhance the heat transfer from the melt to the particle, and therefore, the particle melts easily [107]. Literature shows decreasing particle size (decrease in mass) is energetically efficient as less requirement of heat for melting [107]. Factors such as method of powder production, oxygen concentration in powder effect the powder deposition during laser processing. It is reported that water-atomized 316L stainless steel powder

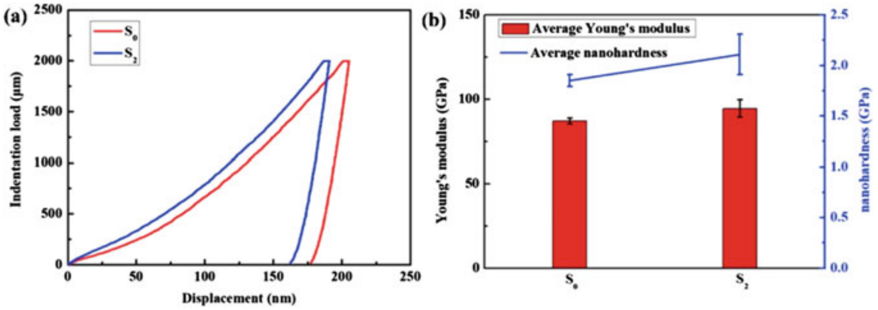

Fig. 10 **a** Indentation load and displacement plot, **b** average Young's modulus and nanohardness of without (S_0) and 2 wt.% nano SiC (S_2) added AlSi7Mg alloy, Reprinted from J. Alloys Compd., **810**, Wang, M., Song, B., Wei, Q., Shi, Y., Improved mechanical properties of AlSi7Mg/nano–SiCp composites fabricated by selective laser melting. 151926, Copyright (2019) with permission from Elsevier [91]

provides enhanced surface quality, homogeneity, layer bonding, however with higher deposition time than gas-atomized powder [108].

5 Applications and Prospects of AM Products with Introduction of Nanomaterials

AM products produced by the addition of nanomaterials is already illustrated in brief. The commercial application domain of AM is quite extensive. However, technological requirements and challenges for each application need to be addressed to become potential manufacturer in AM industry in view of Industry 4.0 [105]. The complexity of product design, economical perspectives are also major points to concentrate for long-range sustainability. The attributes contributing to the cost in AM of the overall production cost can be ranked as [105, 109]:

(a) AM machine cost (50–75%)
(b) Materials cost (20–40%)
(c) Labour cost (5–30%).

The viability of AM depends on the product cost and complex shape fabrication in the competitive market. Some of the applications of nanomaterials induced AM-based products are listed in Table 1.

As presented in Table 1, nanomaterials are extensive utilized in additive manufacturing process. Process parameters of AM (during synthesis) can be tailored to minimize product defects and enrichment of properties. Liu et al. have showed the application of SiO_2 and Metal–organic frameworks (MOF) nanoparticles for development of stratified porous ceramics by direct ink writing (DIW) method for waste

Table 1 Nanomaterials used in different AM technique and final applications

Type of nanomaterials	AM method	Applications	References
Cu nanoparticle ink	Microscale selective laser sintering	Microelectronics packaging	[110]
Au nanoparticles	Inkjet printing	Evaluating water quality	[111]
Ag nanoparticles, styrene-b-butadiene-b-styrene (SBS) film	3D printing	Electrochemiluminescence (ECL) device	[112]
Calcium phosphate (Ca–P), carbonated hydroxyapatite (chap) nanoparticles	Selective laser sintering	Bone tissue engineering scaffolds	[113]
Thermoplastic polyurethane, multiwalled carbon nanotube	3D printing (Fused deposition modelling)	Strain sensing	[114]
Ag nanoparticles	3D printing	Electrodes (for Li ion batteries), Electrochemical energy storage	[115]
MnO_2 nanosheet	Hydrothermal growth of MnO_2 on 3D printed graphene aerogel	Supercapacitor electrodes	[116]
Bi_2Te_3 nanowires	Inkjet printing	Thermoelectric generators	[117]
SiO_2 nanoparticle ink	3D printing	Tissue engineering, nanomedicine	[118]

water treatment (Fig. 11) [119]. Development of MOF on the ceramic structure has been carried out by hydrothermal process [119].

6 Conclusions

Additive manufacturing is a state-of-the-art technique to produce components and intricate designs. The chapter summarises that the addition of nanomaterials in different additive manufacturing methods with controlled size, shape, surface roughness, flowability, wettability can improve the uniformity during deposition and bulk product properties. However, the achievement of the above properties depends on the appropriate selection of nanomaterial synthesis route, 3D printing method, and process control parameters. From the above discussion, it is also realized that reduction of agglomerates of nanomaterials is a necessary condition for successful product fabrication. It is also directed that functionalization of nanomaterials is a major requirement for extension of commercial application of AM products. Functional ink of nanomaterial provides a cost effective strategy of mass scale sensor production by AM [8]. Even, engineered nanomaterials can be utilized to decrease water

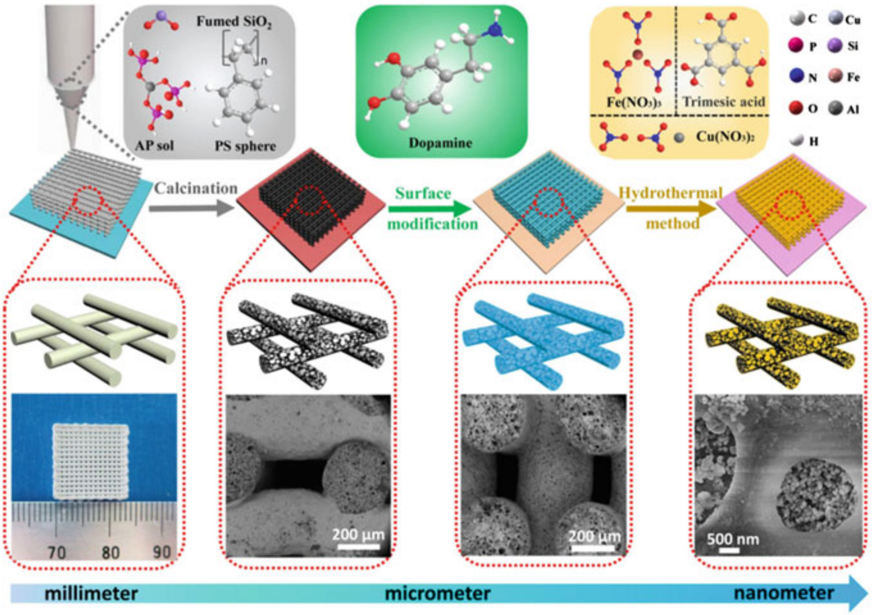

Fig. 11 Stratified porous ceramics developed by direct ink writing, Reprinted from Chem. Eng. J., **397**, Liu, D., Jiang, P., Li, X., Liu, J., Zhou, L., Wang, X., Zhou, F., 3D printing of metal–organic frameworks decorated hierarchical porous ceramics for high-efficiency catalytic degradation. 125392, Copyright (2020) with permission from Elsevier [119]

contamination, wastage and energy [120]. Therefore, finally, it can be concluded that functional nanomaterials incorporated in AM can be a strong candidate for sustainable product development.

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Chapter 4
Metal Based Additive Manufacturing

Umit Dasdemir and Emre Altas

Abstract Additive Manufacturing is a common name used for manufacturing methods that fabricate the desired part by layer-upon-layer. There is a variety of materials that can be processed by AM technologies such as polymer, metal, ceramic, biomaterial, and even concrete. Due to their superiorities, AM applications in many industries are becoming widespread. AM technologies are classified into seven groups and four of them are well suited for metal feedstock material processing. Powder Bed Fusion (PBF) uses either a laser or an electron beam as an energy source to fuse powder particles. Selective Laser Melting and Electron Beam Melting are common PBF technologies. Direct Energy Deposition is another process where the energy source generates a melt pool, and the feedstock material is deposited inside the melt pool simultaneously. In Binder Jetting, a printhead deposits a binding agent to bind powder particles together, and post-processing is required to strengthen the fabricated part. This chapter provides the working principle, main machine parts, general process parameters, materials used, and advantages and disadvantages of each technology.

Keywords Additive manufacturing · Selective laser · Electron beam · Melting · Direct energy deposition · Binder jetting

Abbreviations

AM	Additive Manufacturing
BJ	Binder Jetting

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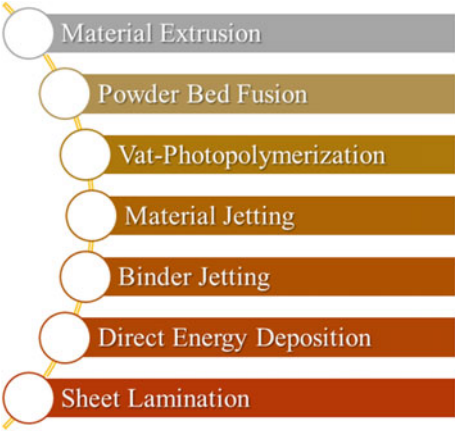
CIP	Cold Isostatic Pressing
CNC	Computer Numerical Control
EDM	Electrical Discharge Machining
DED	Direct Energy Deposition
DMD	Direct Metal Deposition
DMLM	Direct Metal Laser Melting
DMP	Direct Metal Printing
EBM	Electron Beam Melting
EBAM	Electron Beam Additive Manufacturing
EBF3	Electron Beam FreeForm Fabrication
HIP	Hot Isostatic Pressing
LENS	Laser Engineered Net Shaping
LPBF	Laser Powder Bed Fusion
MFR	Material Feeding Rate
MJ	Material Jetting
PBF	Powder Bed Fusion
SLS	Selective Laser Sintering
SLM	Selective Laser Melting
UAM	Ultrasonic Additive Manufacturing
WAAM	Wire Arc Additive Manufacturing

1 Introduction

Today, the manufacturing industry is in motion to adopt a smart and dynamic production that is one of the basic elements of the industrial revolution. Additive manufacturing is a general name of a group of nonconventional manufacturing methods that are based on producing the desired 3D part layer by layer and enable the production of complex geometries that cannot be produced by conventional methods. AM is prone to minimize the waste of raw materials, and eliminate the cost of mold, equipment, and stock. According to the American Society for Testing and Materials standards, additive manufacturing methods are categorized into seven main technologies given in Fig. 1 [1, 2].

While primitive additive manufacturing technologies were able to process generally polymer-based materials due to technological limitations, metallic materials can be widely used in current technologies thanks to recent developments. Powder Bed Fusion (PBF), Binder Jetting (BJ), Direct Energy Deposition (DED) and Sheet Lamination are well suited for metal feedstock material processing. PBF is the most common AM process used with metal materials and is based on fusing powder particles selectively by an energy source to fabricate 3D components. DED uses an energy source to generate a melt pool and melting feedstock material that is being deposited. The feedstock material can be in a form of powder or wire. BJ is another process in which a printhead selectively deposits a binding agent over a powder bed to bind

Fig. 1 The seven main additive manufacturing technologies



them together and then the post-processing is needed to improve the final part properties. Sheet lamination bonds thin metal sheets together and the bonded metal stack is cut by subtractive manufacturing technologies to give the final form [3, 4].

Metal AM enables the production of very detailed components accurately. Lighter and stronger parts can be fabricated due to the layer upon layer manufacturing phenomenon. Reducing or eliminating the need for tools and assembly offers more flexible, faster, customized, and cost-effective manufacturing with greater efficiency. The aerospace industry is one of the first to adopt metal AM and the adoption by many industries shows a growing trend through these superiorities. Some of these industries are shown in Fig. 2 [5, 6].

Metal additive manufacturing technologies are divided into two different categories: fusion-based where the feedstock material is fully fused to create the sliced layer and non-fusion-based. Fused-based technologies can also be grouped into two

Fig. 2 Industries that currently use metal AM technologies

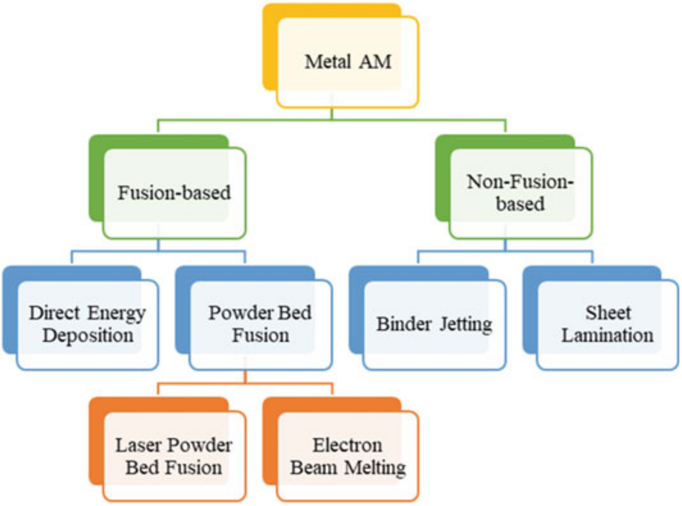


Fig. 3 The classification of metal additive manufacturing technologies

categories that are powder bed fusion and feedstock fed fusion. Figure 3 shows metal additive manufacturing classification [4].

2 Powder Bed Fusion Technologies

Powder Bed Fusion (PBF) is one of the earliest additive manufacturing processes based on selectively fusion of the feedstock material in a form of powder by energy source such as laser or electron beam. Selective Laser Sintering (SLS), Selective Laser Melting (SLM), and Electron Beam Melting (EBM) are powder bed fusion processes. Metal powder bed fusion systems currently tend to melt the powder particles instead of sintering to build nearly full density part [7].

2.1 Laser Powder Bed Fusion (SLM)

Laser powder bed fusion is one of the first commercialized, most common, and extended additive manufacturing technology that places its origin back to the research made by researchers at the University of Texas at Austin in the 1980s. Carl Deckard filed a patent in 1989 and it was commercialized by 3D Systems. Since then, the process has had exponential growth in terms of the machines provided, the materials used, and the industries applied. Laser Powder Bed Fusion is alternatively known as Selective Laser Melting (SLM), Direct Metal Laser Melting (DMLM), and

Direct Metal Printing (DMP). EOS (Germany), SLM Solutions (Germany), Concept Laser (Germany), Renishaw (UK), and 3D Systems (France/USA) are the major shareholders of the LPBF market.

The energy source system (beam generation and manipulation), powder feeding system, enclosed chamber, build platform, and controlling system are the main parts of the SLM machine. The energy system is made up of a laser that is currently a fiber laser and scanning optics that enable to focus of the laser beam over the build platform. Most of the LPBF commercially available in the market come with fiber laser that works in a wavelength of 1064 nm and increases absorption rate. The gas laser was used as an energy source in an early version of the machine and the conversion rate of the input power to useful power has increased from around 20% up to 80% by switching gas lasers to fiber lasers. Single mode Ytterbium-Doped Yttrium Aluminum Garnet (Yb:YAG) or Neodymium-Doped Yttrium Aluminum Garnet (Nd:YAG) are common fiber lasers used with Gaussian power distribution [8–10].

The powder feeding system creates the powder layer and holds the fabricated part. Two different powder-feeding systems are available. One of them consists of a powder chamber with a piston where the piston goes up to provide a sufficient amount of powder and the other one is having a hopper over the powder bed. A certain amount of powders fall in front of the rake/roller. The enclosed build chamber ensures that the powder layer is not disturbed during the process by providing a non-oxidation and heated environment. The build platform moves in the z direction to let spreading powder layers and holds the part while it is being fabricated. A controlling system that has a high-speed camera or temperature sensor can be placed into the build chamber to image the melt pool for in-situ process monitoring. Laser power, number of lasers, powder handling system, scanning strategies, and build volume are differentiated over the years [11–13].

The build bed leveling must be primarily carried out to ensure anchoring the very first fabricated layer to the build bed. The LPBF process starts with spreading a predefined thickness of the powder layer by a rake/roller over the built plate. Then the laser is focused by a controlled scanning mirror to selectively melt the powder. When the resolidification of the first molten layer is done, the build platform goes down in the z direction and the fresh powder layer is overspread. These steps are repeated over again till the final part is fully fabricated.

A melt pool is the molten metal area that occurs from the interaction between the energy source and the feedstock material. The level of the energy density defines these variables that affect the temperature gradient and the solidification rate. The temperature gradient and the solidification rate determine the microstructure, thereby affecting the mechanical properties of the final part. Laser exposure is generally adjusted to provide a certain depth into the previous layer that is also melted and hence the full fusion of each layer into the previous is procured. As a result, the properties of the completely fabricated part are less directional [14–16].

The enclosed chamber and the build platform are heated to minimize the temperature differences between the pre-laid powder layer and the high-energy laser beam. Preheating minimizes the required laser power for the process, and the formation of residual stress, shrinkage, and distortion. Lower preheat up to 400 °C is beneficial for easily removing unmolten powder surrounding the fabricated part and reusing that powder. To have efficient preheating for large parts, some machines are equipped with radiators above the build platform. Excessive preheating may cause over-sintering of surrounding powder and oxidation. Surrounding gasses such as oxygen can cause several gas defects and oxidation of the melt pool. The whole process is performed under a protected atmosphere. A flow gas such as nitrogen(N) or argon (Ar) is pumped into the build chamber to prevent oxidation and to clear the spatter that occurs from the laser path.

Powder particle size distribution (15–63 µm) is finer than Electron Beam Melting (EBM) herewith the thinner layer thickness (15–150 µm) can be attained which is better for surface integrity (Ra 10–20 µm), and higher precision but also results in longer production time and higher cost. The desired properties of the powders are good spherical, fine particle size distribution, homogeneous composition, non-contaminated, and low intraparticle porosity. Before modern metal LPBF machines adopted fully fused metal powders, metal powder coated with binder polymer is used by liquid phase sintering. Stainless steel (316L, 17-4PH), titanium alloys (TiAl6V4), nickel-based alloys (Inconel 625/718), Al alloys (AlSi10Mg), and CoCrMo are common materials for SLM technology. Precious metals such as silver and gold can also be processed by SLM for jewelry industry applications [11, 17].

The usage of multi-lasers that enable scanning different regions simultaneously becomes evident. Thanks to these developments, the production rate is improved by reducing lead time and cost. Working at low temperatures provides easier powder removal, especially from the inner geometries and recycling of non-sintered powder surrounding the fabricated part. Very complex inner geometries can be manufactured. It can produce a denser product than conventional powder metallurgy. SLM is the best-suited method for producing titanium alloys since it is hard to produce by conventional manufacturing systems [9, 18].

High thermal conductivity, high surface tension, high laser reflectivity, and propensity to oxidize the metal materials made them difficult to process. Development in laser technologies and presenting fiber lasers with wavelength increased the absorptivity of metal powders and enabled metal PBF processing. Unlike SLS, SLM needs a support structure and the support structure needed in LPBF is denser than in EBM due to lower process temperature conditions and very fast cooling rates [2, 19].

Scanning strategies affect the properties of the fabricated part including density, residual stress, and then mechanical properties. Some different scanning technologies are adopted by SLM machine vendors, such as line-wise scanning throughout the x-axis or the y-axis or area-wise island scanning where the layers are divided into small squares and randomly melted afterward to avoid accumulating the energy in specific areas of the sliced geometry. Island scanning is a better choice to reduce the effect of the swelling phenomenon [20, 21].

The cost efficiency, near-net-shaped part production, increased functionality, and wide range of materials that can be used are the main advantages of the SLM process. SLM is a relatively slow process due to scan speed, and parameter optimization is also time-consuming. Printable size limitation, high power usage, and difficulties in powder handling are some other drawbacks of SLM. Fabricated parts may have rough surface roughness depending on powder size, layer thickness, and process parameters. Build direction may cause anisotropy in the microstructure. High process temperature increases the possibility of residual stress and crack formation. SLM is one of the best methods for metal feedstock processing and in getting more accessible to manufacturers [3, 13, 22].

2.2 Electron Beam Powder Bed Fusion (EBM)

Electron beam-based powder bed fusion was developed at Chalmers University of Technology and was commercialized by a Swedish company named ARCAM which is currently owned by GE in 2002. Until quite recently, ARCAM was the only stakeholder in the EBM market and there are some other companies started to develop their technologies these days. However, 90% of the machines are still provided by ARCAM. EBM is extensively used in the manufacturing of turbine blades, engine components, and biomedical implants. Parts are fabricated by fusing metal powder with a high-energy electron beam in a high vacuum environment [3, 18].

An EBM machine generally consists of four different sections that are beam generation system, beam manipulation system, vacuum chamber, and powder bed system [13].

Beam Generation System: A high-energy electron beam is used as a thermal source to induce fusion between metal powder particles. Thus, the lack of fusion is almost eliminated by using a high-energy electron beam instead of a laser beam and it has the highest efficiency that electron beam power to the input power is around 95%. This efficiency is 10–20% with CO_2 laser, around 80% with fiber laser in SLM, and the remaining energy is lost in form of heat. Electrons are emitted by heating a cathode filament and are subjected to an accelerated voltage to generate a high-energy electron beam. Cathode material should have a high melting point to not be melted during the beam generation and a low work function that ensures electron detaching at a low voltage state. An early version of the machines had Tungsten cathode filament but these days Lanthanum Hexaboride (LaB6) or Cerium Hexaboride (CeB6) are used due to their higher melting point, and lower work function properties [3, 4, 23].

Beam Manipulation System: The generated beam passes through different electromagnetic coils to correct astigmatism, deflect the beam to generate trajectories, and then focus the beam on a build platform [3, 23].

Vacuum System: During the process; the vacuum is needed to prevent interaction between the electrons, and air molecules which cause ionization of molecules and hence loss in energy, process speed, and the direction of the electrons. Reducing the oxidation of the reactive materials caused by reactive gases such as oxygen during the process is another advantage of the vacuum since the presence of an oxide layer on the surface decreases electrical conductivity [4, 23].

Interaction between electrons and pre-layered powders causes electron transfer through the powder particles and charging them. Negative charge accumulation in the powder bed may destabilize particles' positions. To avoid damaging the layer formation caused by destabilized powder position, a low atomic numbered gas such as Helium (He) is used to discharge the charged powder particles. He is introduced into the chamber to maintain constant pressure to limit this electrostatic phenomenon. The vacuum should be carefully carried out during the process. Unsuitable vacuuming may decrease the melting point of metals. During the metal alloy processing, the metal that has a lower melting point will have a higher rate of evaporation which means higher loss and results in the change of final alloy composition. It also takes time to create a vacuum which affects the production rate. That is the reason why the vacuum should be sufficiently determined. In ARCAM approximately a vacuum of 10^{-5} mbar is pulled around 30 min [4, 9, 18].

Optical cameras and infrared thermography can be used for in-situ process monitoring. The heat energy that is needed for the fusion of powders is produced on account of the high kinetic energy of the electrons. (in SLM, regarded as to the process of photon absorption.) During the EBM process, each layer undergoes a period of preheating to provide the same average temperature at each layer and to achieve a slight sintering between powder particles. This sintering provided by preheating assists to increase the electrical conductivity, discharging the electrical charges, and avoiding smoke formation. A flow of negative charges can be concentrated in the powder particles and the particles will be negatively charged if the electrical conduction is insufficient. When the repulsive electrostatic forces become greater than gravitational and Van der Waals forces, a powder cloud formation takes part inside the build chamber that causes a sudden stop of the process [9, 18, 24].

Preheating is required after the layer formation to provide attachment of powder to the build plate or previously deposited layer. Attachment may be provided by sintering (joined by forming a neck through the diffusion of atoms). Thus, electron accumulation in the powders can be prevented. Neck formation during sintering increases the electrical conductivity and contact between the powder and build plate enhanced by neck formation results in the dissipation of electrical charges to the ground. A defocused beam sweeps across the pre-laid powder layer a few times at high power and speed to heat the build platform uniformly up to preset temperature according to material properties. Preheating temperature depends on the feedstock material and characteristics of the powders such as density, size, and electrical and thermal conductivity. Significantly different microstructure from the other metal AM is attained in EBM by means of preheating. The obtained microstructure is coarser than the one obtained by SLM and similar to the cast microstructure with less porosity [18, 25–27].

The inability to process non-conductive materials is the main drawback of EBM technology. There will not be any interaction between the powder and the electron beam. In such circumstances, negative charge accumulation in a certain area increases electrostatic forces. When the electrostatic forces overcome the gravitational force, rapid expulsion and deflection occur. As a result of that, the fabrication is failed [9, 26].

Powders need to have spherical morphology, isolated particles, and similar size distribution for homogeneous powder spreading to obtain a stable process. The lower particle diameter causes smoke phenomena and the higher one results in poor surface finishing. Size distribution of 40–100 μm is common. Typical layer thickness is from 50 to 200 μm. surface roughness obtained is between 20 and 40 μm. production rate is between 70 and 100 $\text{cm}^3\ \text{h}^{-1}$. The fabricated part has an excellent density of 99.9%. The feedstock cost of EBM is slightly lower than SLM technology since the particle size distribution is higher. Stainless steel, titanium alloys, tantalum, cobalt alloys, nickel alloys, and copper alloys can be processed by EBM [11, 17, 18].

ARCAM claims that EBM fabricated part properties are better than cast and comparable to wrought. The slow cooling rate provides more time for grain growth and relaxation of the microstructure that both reduce shrinkage, distortion and residual stress. The residual stresses that occurred in the EBM process are much lower than SLM. On the other hand, a long cooling cycle may cause oxidation and interstitial contaminant diffusion on highly reactive materials. Multiple melt pools can be generated simultaneously, and more than one part can be fabricated at a build cycle. The production rate of EBM is much higher than SLM due to high electron beam speed and higher layer thickness due to larger particle size distribution [16, 28].

Dimensional accuracy and surface integrity are influenced negatively due to the larger particle size and focal conditions. Preheating causes sintering of the surrounding powder of the fabricated part which increases the cleaning process time and therefore the cost. Slightly sintering of the surrounding powder by preheating provides support to the fabricated part and reduces the need for a rigid support structure. This sintered support structure is more easily removed and recycled during postprocessing. To provide electrical conduction and eliminate electron charging, support between the powder bed and base plate is used. This needed support is much smaller than the one needed in SLM. The general comparison of SLM and EBM methods is given in Table 1 [16].

2.3 Main Process Parameters of Powder Bed Fusion

There are several process parameters that are illustrated influence the production rate, cost, and the properties of the fabricated part such as surface roughness, density, mechanical properties and residual stress. The main parameters can be grouped into four: energy source-related, scan-related, powder-related, and temperature-related [3, 29].

Scan speed and *beam energy* are related as Eq. 1,

$$E = \frac{(P)}{(S)(V)(L)} \tag{1}$$

Table 1 Comparison of SLM and EBM

	SLM	EBM
Source of energy	Laser beam	Electron beam
Process atmosphere	Inert gas	Vacuum
Absorption limiting	Absorptivity	Conductivity
Process limiting	Spreadibility	Smoking effect
Preheat temperature	Up to 400 °C	Up to 800 °C
Powder particle size (µm)	15–63	15–104
Layer thickness (µm)	15–150	20–60
Scan speed	Moderate	High
Build rate	1	1.5–2 times higher than SLM
Surface integrity	High	Moderate
Precision	High	Moderate

where E is beam energy density, P is beam power, S is spot size, V is scan speed, and L is layer thickness. Increasing *beam power* decreases the possibility of porosity formation but exceeded beam power may cause the previously printed layers. Lower beam power causes insufficient melting of powder particles. Increasing scan speed or spot size will decrease the energy density that may not be sufficient to fuse the powder particle. Increasing the power may look like a solution for that problem but increasing scan speed and the beam power will decrease the exposure time that causes insufficient melting. Scan speed determines melt pool length, higher scan speed means a longer and thinner melt pool that cause balling effect and delamination between the layers [4, 30].

Hatch spacing is the distance between the centers of two adjacent laser scans and is directly proportional to the production rate. If the hatch spacing is high, a smaller number of scanning along the whole layer is needed which means less time to scan the whole layer. If the sufficient laser *spot size* which is the focal diameter of the beam is not provided for a large hatch spacing, the gap between two consecutive scans will be remained causing porosity inside the fabricated part. To avoid this defect, there should be an overlap between scans. Due to the Gaussian beam, power at the center of the scan will be higher than the boundaries. The overlap will also compensate for this less heat generation at the boundaries [31].

Scanning strategy is the moving pattern of the energy source during the process and varies by direction, sequence, vector length, and rotation angle. Scanning strategy has a considerable influence on the thermal gradient and hence residual stress, balling effect, and the properties of the final part. Particle size, shape, and distribution affect the spreadability of powder material and the surface integrity of the completely fabricated part. The final part density is directly proportional to the powder bed density and a high density of powder bed is preferred to have near full density part [3, 4, 32].

Layer thickness is a preliminary parameter that directly affects the production rate. Increasing the layer thickness increases the production rate. However, higher precision can be obtained with a low layer thickness. Even though processing the thicker layer requires higher laser energy, the level of practicable laser energy is limited. High laser energy may cause distortion on the fabricated part and can be avoided by scanning the same surface more than once with lower energy. Besides the thin layer thickness allowing more dense parts and better surface integrity, it requires lower energy density to be fully fused. Lower shrinkage and hence dimensional accuracy may be obtained by lower layer thickness. For the lower layer thickness, small particle size distribution is needed, which increases fabrication time and the cost of the part [4, 30, 31].

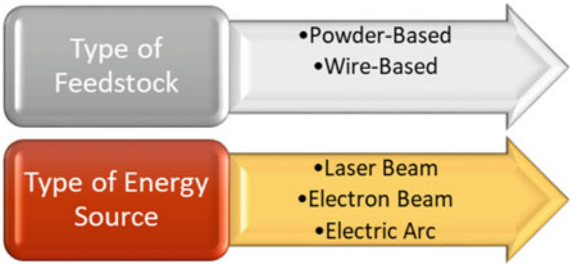
3 Direct Energy Deposition

The general process of Direct Energy Deposition (DED) also known as Direct Metal Deposition (DMD), Laser Engineered Net Shape (LENS), and Electron Beam Freeform Fabrication (EBF3) consists of focusing direct energy into a narrow region over a build plate or pre-built part to generate a melt pool and simultaneously melting feedstock material that is being deposited into the melt pool. The main difference between DED and PBF is not melting a pre-laid powder layer but melting the feedstock material as it is being deposited it has similar process characteristics with laser cladding and the 5-axis laser welding. The DED process is predominantly used for metal materials and can be performed to add a feature to a pre-built component, for repairs, or occasionally to fabricate a new part [9, 12].

Different types of DED technologies are commercially available depending on the heat source and the material feeding mechanism used and users can pick the optimal configuration for their application (Fig. 4). The feedstock material can be in a form of powder or wire. A laser beam, electron beam, and electric arc are the energy sources that are used in commercially available machines [13].

The laser beam that has a smaller beam diameter enables finer feature production. The electron beam has a relatively large beam diameter to avoid charge accumulation and provide a larger production rate. Laser beam-based DED has the fastest cooling

Fig. 4 Classification of DED according to feedstock and energy source types



rate resulting in fine microstructure and hence improved strength. The cooling stage is longer in electron beam-based systems and the larger heat that is generated by the electric arc contributes even longer cooling cycle that increases the residual stress [9, 13].

A eposition head consists of laser optics, a feedstock nozzle, inert gas tubing and sometimes controlling sensors. The deposition process can be controlled by the motion between the deposition head and the substrate. This motion can be obtained by moving only the deposition head, moving only the substrate, or movement of both. There are a few companies that provide deposition heads as a CNC milling tool that enables additive and subtractive manufacturing consecutively which is beneficial for repairing and better dimensional tolerances. A nonvertical deposition is as effective as a vertical one due to the kinetic energy of powder particles fed into the melt pool is greater than the gravitational force of the powder particles. This feature makes multi-axis deposition possible [3, 33].

The building part process involves deposition, melting, and solidification of the feedstock material. The energy source generates a melt pool on the desired area of the substrate that can be either built plate to fabricate e new part or a pre-built component to add an additional section or to overhaul and repair. The feedstock material is fed into the melt pool when it is fully melted and then solidified as the energy source passes. When a layer is completed, the nozzle and/or substrate moves by the thickness of one layer to enable the deposition of the next layer. These steps consecutively repeat until the desired part is fully completed [3, 4, 26].

The feedstock can be used in a powder or wire form in DED. A powder-based feedstock is used for laser or arc-based energy source systems and wire-based feedstock can be used for all energy sources. The wire form of many alloys is available and is suitable for many applications where the lower dimensional accuracy is not an issue or full density is the main requirement. The feedstock capture efficiency is almost 100% in the wire-based feedstock. It is mostly suitable for less detailed geometries and surface coating. To provide uniform beads during the deposition, the wire diameter that varies between 0.9 and 4 mm stability is significant. 316 stainless steel, Inconel 625, and Ti6Al4V are commonly used in DED technologies [33]. Powder form material is more flexible and it can be mixed while depositing which provides composition changing and multi-material part fabrication. The main drawbacks of powder are a transition between the materials and the deposition rate of powder into the melt pool (around 50–90% of powder is deposited into the melt pool). In wire-based feedstock material, the material feeding rate (MFR) is well defined. On the other hand, depositing more than one wire simultaneously is not easy [13, 18].

DED is a very complex manufacturing process that depends on many process parameters given in Fig. 5. Geometry-related process parameters should be controlled for complex geometry [13, 34].

DED is the most suitable additive manufacturing process for repairing and feature adding due to the 5 or more axis systems. Nearly full-density parts with a minimum level of porosity can be fabricated by the DED method. DED machines have a larger build envelope than PBF and directing material by a nozzle instead of requiring a powder bed allows building larger parts and are suitable for automotive and aerospace

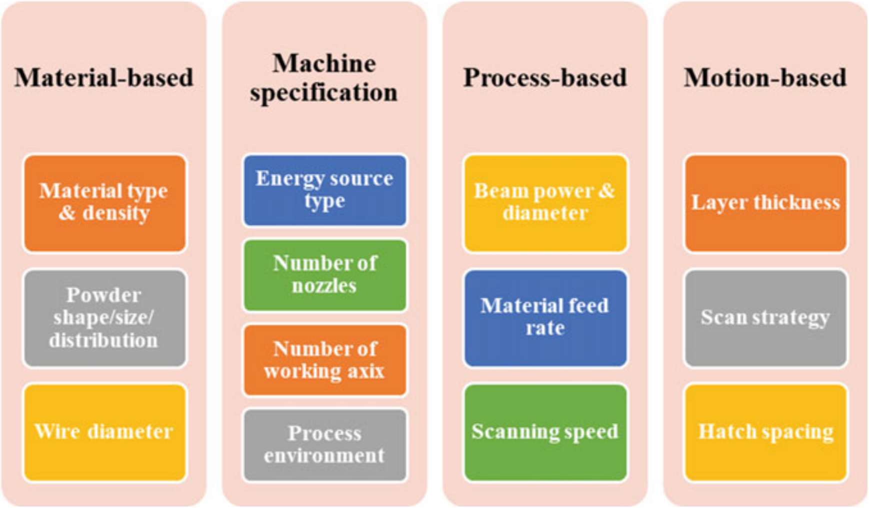


Fig. 5 The main DED process properties

industry applications. Build envelope can be expanded by taking advantage of robotic systems. DED offers one of the highest deposition rates among AM technologies. The deposition rate can be in the range of 500 to 4000 cm^3/h depending on the energy source type. Due to directly infusing the material into the melt pool, particle size distribution and morphology of the powder material is not a requirement. Compared to PBF, DED can be processed wider range of materials. It is easier to introduce second material by adding a second nozzle to the printhead [13, 18, 34].

Complex geometries and internal features may not be achievable with DED due to a lower level of resolution compared to PBF. A support structure or a multi-axis deposition head is required for geometry complexity. The material delivery nozzle and the energy source move together causing slower beam scanning and over-deposition at corners may occur that negatively affects the dimensional accuracy. The completed part requires machining to obtain desired tolerances/surface integrity and heat treatment to compensate for the residual stress caused by a large melt pool. However, it is an unsuitable process for temperature-sensitive materials such as aluminum, and magnesium due to high process temperature [3, 9, 13].

Laser Engineered Net Shaping (LENS) is one of the first commercialized DED processes. It was developed at Sandia National Laboratories and commercialized by Optomec, USA in 1997. In this DED type of manufacturing method, the feedstock material is in powder form and the energy source is a high-power laser beam. The process takes place under an inert gas environment to avoid melt pool oxidation [35, 36].

Electron Beam Additive Manufacturing (EBAM) consists of fabricating desired parts by feeding the feedstock material into a melt pool generated by an electron beam.

Skiacky, the USA is the only vendor that offers wire based EBAM. NASA has similar technology known as Electron Beam Freeform Fabrication (EBF3). Interaction between wire, electron beam, and build plate/part takes place in a vacuum environment to ensure the focusing of an electron beam. EBAM is a highly efficient process due to the maximum material fed and 95% conversion rate of the electron beam [16].

Wire Arc Additive Manufacturing (WAAM) uses metal wire as feedstock material and electric arc as an energy source. An electric arc melts the metal wire as it is deposited, and inert gas is used to prevent oxidation and control the metal's properties. WAAM is increasingly applied for repairing. No support structure is needed for the process. CNC machining can be performed for better surface roughness and dimensional accuracy and heat treatment application for residual stress relief. The process does not require a vacuum chamber and is the most cost-effective DED process especially for fabricating a large part. MX3D (Netherlands), WAAM3D (UK), Gefertec (Germany), and Norsk Titanium (Norway) are companies that commercially offer WAAM machines [37, 38].

4 Binder Jetting

Binder Jetting (BJ) is one of the non-fusion metal additive manufacturing technologies. It was first invented at the Massachusetts Institute of Technology in 1993 as 3D Printing and patented by Z Corp in 1995. ExOne, 3D Systems, Sintertek, Voxeljet, GE, and HP are currently launching commercial machines and ExOne is a pioneer vendor in the BJ technology market. The technology was first developed for polymer-based materials and then metallic materials are widely adopted. Numerous technological advancements have taken place since the first BJ machine came up and it is becoming so popular in metal additive manufacturing in recent years. A very high production rate, the detailed feature production capability of around 99.5% density, and a wide range of materials that can be used are the main benefits of this technology. That is the reason why, many companies launch their own BJ machines, even though BJ is not widespread yet [39, 40].

The BJ machine consists of a powder handling system that spreads a fine powder layer, a binder jetting head with multiple inkjets that deposit binder droplets to join metal particles, and a curing system to polymerize the binding agents. The smallest build area with a dimension of 165 mm width × 65 mm depth × 65 mm height is offered by ExOne and Voxeljet launched a BJ machine with the largest build area with a dimension of 4000 mm W × 2000 mm D × 1000 mm. More than one part can be built at a time [13, 26, 41].

In this technology, the desired part is printed layer by layer on a powder bed like PBF. On the other hand, there is no thermal energy source to fuse the particle which is the main process in PBF technology. The particles are bounded together by the help of dispensing binding agent using an inkjet printhead similar to Material

Jetting (MJ). However, the binding agent is just a small portion of the part, and it will be evaporated in the post-processing stage in contrast to the MJ. BJ is an indirect additive manufacturing process that takes place in two main stages. The first stage is creating the green part which means giving the component its shape. The second step is *sintering* and/or *infiltration* of the green part to give the component final properties. The main process consists of green part fabrication, curing, depowdering, debinding, sintering, and/or infiltration [13, 18, 42].

The inkjet printhead with multiple nozzles passes over the pre-laid powder layer and dispenses very small droplets of polymer-based aqueous binding agent to bind metal powder particles together. Binding occurs at room or very low temperatures and metal powder particles are not melted, so the thermal-related defects such as residual stress, distortion, and shrinkage are eliminated. Besides, inert gas or vacuum environment is not needed. The build platform moves down as much as layer thickness and a fresh powder layer is overspread by roller/rake. During the green part fabrication, the chamber temperature can be controlled to provide partial drying of the printed layers to avoid slippage when the new layer is deposited. [13, 26].

As soon as the green part fabrication is over, the curing stage where the infrared heater subjects the heat takes place for a few hours to have binding in the binder-saturated area completely. The green part obtained is a nearly full dense composite of base metal and binding agent that is filling the pores between metal powder particles. The minimum mechanical properties are established. It also has significant porosity and a brittle structure. The cured green part is extracted from the powder bed (depowdering stage) and gently cleaned to remove the surrounding loose powder by pressured air. The cellular structure might be a problem during transferring the brittle green part to the furnace [3, 9, 26].

Post-processing applied after the green part fabrication consists of binding agent removal, solid-state sintering, and infiltration to strengthen the part before using. The majority of the manufacturing lead time is spent during the post-processing. The fabricated, cured, and depowdered green part is placed into a furnace to heat up to the sintering temperature resulting in evaporation of the binding agent (debinding stage) and providing partial particle sintering. The sintering process takes place in two consecutive cycles, a low-temperature cycle in the furnace to burn off the polymer binding agent and a high-temperature cycle for solid-state sintering of metal particles. At the end of the first cycle, the brittle green part with a high degree of porosity is obtained. In the second cycle, the sintering process is continued to decrease the density of porosity and/or infiltration with a lower melting point liquid metal that is different than base metal takes place to fill the pores [3, 4, 42].

During the sintering process, the atomic diffusion is sufficiently activated resulting in densification and hence shrinkage is inevitable. High dimensional shrinkage and high sintering temperature make it difficult to work with tight tolerances. Current tolerances are in the range of 0.1–0.2 mm at best. The shrinkage rate that is nearly homogeneous linear dimensional with a rate of around 15% should be considered at the design stage to ensure desired dimensional accuracy. Controlling the dimensional shrinkage is a major challenge and requires advanced knowledge in powder metallurgy and sintering behaviors of metallic powders. A master sintering curve should be developed to identify the sintering conditions [18, 42].

Infiltration is another post-processing based on filling a porous body with liquid infiltrant. Metal infiltrant must have a lower melting point. Infiltration after some amount of sintering ends up with lower shrinkage and also metal matrix–metal powder composite parts with specifically engineered properties can be manufactured. Near-full dense single-material components can be fabricated by using new materials developed for BJ technology and controlling the sintering process. In this case, the infiltration stage can be skipped [3, 13, 42].

If porosity is a desired property that can be beneficial for some applications such as implants and structural parts, BJ is an excellent metal additive manufacturing method. The degree of porosity can be controlled by monitoring the powder bed density and binding agent saturation. Up to 95% density can be achieved with BJ and Hot Isostatic Pressing (HIP) is one of the most common post-processing methods to decrease the degree of porosity without infiltration. BJ method consists of forming the cross-section of the 3D part on each layer by a few passes of the printhead instead of following a raster path to fuse the particles. That is the reason why BJ is considered a high-speed additive manufacturing process. Surrounding loose powder may act as a support structure and holds up the solidified part overhangs, but metal parts mostly need a support structure to avoid warpage during the sintering process [8, 13, 43].

HP offers a slightly different printing mechanism from other vendors. in this technology named Multi-Jet Fusion, two different binding agents are deposited on each layer. The fusing agent is deposited where the particles need to be bonded together inside the cross-section and the detailing agent is deposited around the fusing agent to determine the border of the cross-section. During the heat source passing over the build bed, powder particles covered by the fusing agent are fused while the particles covered by the detailing agent are unfused. As a result of this process, the finer feature and well-defined edges are provided compared to a regular BJ. Desktop Metal is another BJ machine provider that uses a printhead that can deposit binder droplets with different diameters for better surface integrity and dimensional accuracy. The large droplets fill the interior part of the cross-section when the smaller droplets are dispensed closer to the edges [13].

Printhead speed and binding agent saturation should be optimized to ensure proper bonding and a lower level of porosity. The main process parameters of BJ are given in Fig. 6 [43].

The powders irrespective of their melting points can be processed since the powder particles are not melted during the process. Inconel, Cobalt-Chrome alloys are materials that are difficult to machine with conventional manufacturing and BJ is a promising manufacturing method for processing these materials. Sintered Tungsten carbide, stainless steel (316L), bronze-infiltrated stainless steel, Titanium-alloys (TiAl6V4), and maraging steels are common materials that can be fabricated by BJ. Binding agent material has low viscosity to allow droplets forming and rapidly fall off from the nozzle, stability against large shear stress, good powder interaction, and clean burn-out characteristics [42, 43].

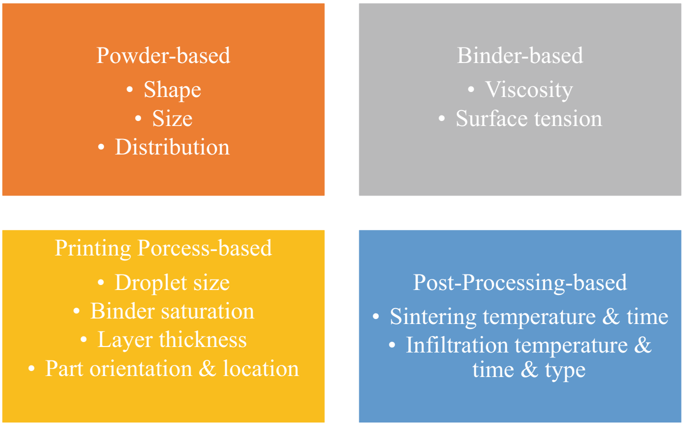


Fig. 6 The main BJ process parameters

Microstructure and mechanical properties depending on the sintering and/or infiltration process are comparable with metal injection molding. BJ is suitable for low to medium-batch production. For instance, injection molding dies can be manufactured. Even though sintering and/or infiltration is costly, the whole process is cost-effective compared to PBF due to not using a laser or electron beam. Materials with poor weldability that makes them difficult to fabricate by PBF, can be printed in BJ [18, 44].

Binder Jetting is a multi-step process that requires additional equipment and increases the production time & cost. Due to brittleness in the green state, manual depowdering may be required. The component fabricated by BJ has poorer mechanical properties compared to PBF and DED due to a higher level of porosity that causes stress concentration, crack formation, and consequently fatigue failure. The technology is limited to processing one type of metal powder inside the build chamber. However, functionally graded structures can be produced by infiltration of a different metal than the base metal powder. For instance, annealed 420 stainless steel matrix infiltrated with bronze offered by ExOne provides high mechanical performance, machinability, and weldability. The surface roughness obtained is similar to PBF, but the dimensional accuracy is much worse [13, 43].

5 Sheet Lamination

Sheet lamination is another additive manufacturing process where the desired part is formed by bonding sheet material. Laminated Object Materials used paper sheets as a feedstock and Ultrasonic Additive Manufacturing (UAM) which is another indirect method for metal additive manufacturing are two distinct processes of sheet lamination. Sheet lamination is a process in which additive and subtractive steps are combined to fabricate a 3D part. In an additive step, the sheets of material are bonded together by applying heat or pressure to provide chemical or mechanical bonding. Mechanical or laser cutting follows the formation of the stack to give a final shape in the subtractive step. Layer-by-layer shaping or stack of layers shaping are optional [4, 5, 12].

Ultrasonic Additive Manufacturing consists of welding sheets of metal using ultrasonic welding and removing unwanted material by a mechanical milling process to form desired part geometry. The process is commercialized by Solidica Inc., USA in 2000. An early version of the technology was suitable for processing soft metals such as aluminum due to a 1 kW power system, but the power of the current machines has increased up to 9 kW even stainless steel or Inconel sheets can be processed [3, 45, 46].

A rotating sonotrode that travels along the length of the metal sheet applies a normal force to keep the metal layers together and oscillates at user-set oscillation amplitude to provide ultrasonic welding between the metal sheets. When the deposition of four sheets of metal is completed, the CNC milling head forms the deposited layers according to desired slice contour. This additive-subtractive process follows each other till the desired part is fabricated. The prevalent frequency of oscillation is around 20 kHz. The sheet thickness is generally between 100 and 150 μm [3, 16].

The most important process parameters are travel speed, oscillation amplitude, and the normal force of the sonotrode. The oscillation amplitude determines the amount of ultrasonic energy that affects the bonding formation between the layers. An insufficient amount of energy cause voids between the layers and delamination occurs during the process. An exceeded energy can damage the previously formed layers. A sufficient normal force is required the ensure keeping layers together and that the ultrasonic energy is delivered to the metal sheet. The travel speed of the sonotrode determines the welding exposure time which directly affects the bonding strength. UAM process generally takes place at room temperature, but some metals may require preheating. A sufficient amount of heating of metal sheets provides better bonding by reducing the flow stress of metals [3, 4, 45].

Faster production, low cost, and easy material handling are some of the benefits of sheet lamination. The process enables to produce embed structures into the part such as fibers, wires, and sensors. This feature makes the method suitable for the production of electronic devices and smart structures. Waste of material, anisotropic mechanical properties, and a high tendency for delamination are the drawbacks of the process. Lattice structure fabrication may also be infeasible due to the difficulties of excess material removal [45, 47].

6 Main Defects in Metal AM

Additive manufactural fabricated parts may include some defect that influence the properties of the components. Interaction of gases, lack of fusion unmolten or partially melted powder are the main reasons of the defects. The possible defects are given in Fig. 7 [48, 49].

Lack of fusion is one of the most common metal AM defects that occurs due to the insufficient energy source power. The feedstock material does not fully melt and fuse into the previous layer or adjacent tracks. A poorly fused powder may cause a porosity, delamination, and crack formation. To avoid the lack of fusion, the beam power should be sufficiently arranged to have fully melting. *Balling* is one of the other most concerns in metal additive manufacturing. If the surface tension is greater than wetting between the melt pool and the base plate/previous layer, melt pool forms in ball-shape instead of continuous melting tracks. Balling increases the surface roughness and the level of porosity. Contamination, oxidation, laser power, scan speed and layer thickness affect the probability of balling formation. Lower cooling rate provide a sufficient time for surface tension and increase the tendency of balling. Due to exceeded energy source power, the melt pool depth can be deeper, and the vapor channel occurs. The gas bubbles arising from the evaporation of the metal inside the deep vapor channel cannot reach the top due to higher melt pool diameter, remain inside and pores occur [13, 49, 50].

A high level of beam power can cause a keyhole formation and unstable keyhole may create voids inside the melt. During the atomization of metallic powder, the gas can be trapped inside the particles and may cause the pores inside the fabricated structure. Lowering the level of shielding gas or processing under vacuum may lower the level of *porosity*. Lack of fusion also causes porosity. Beam power, scanning speed, layer thickness and hatch spacing are the main process parameters that can affect porosity formation. Insufficient bonding between layers due to lower energy density

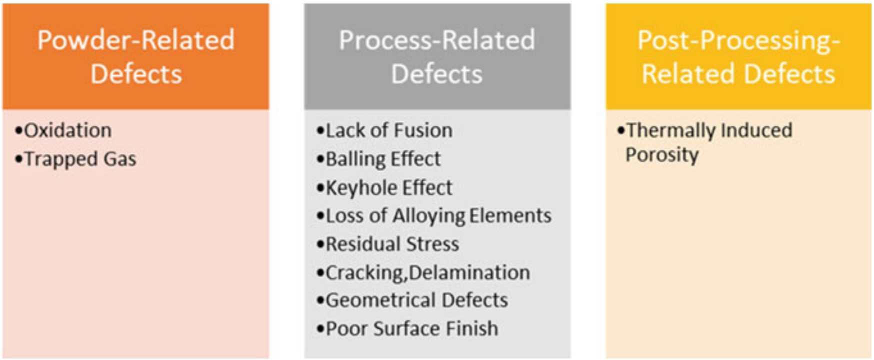


Fig. 7 Defects in metal AM

and the powder characteristic also increases the possibility of porosity formation [13, 51, 52].

Residual stress classified into two different stresses. Uneven heating cause in thermal stress and volume expansion during the phase transformation results in structural stress. Cause in thermal deformation, crack formation and fatigue failure. It also affects the mechanical properties and the dimensional accuracy of the final part. *Cracking* is another defect in additive manufacturing based on lack of bonding. Shrinkage occurs during the cooling stage generates forces resulting in cracks. Impurities also cause crack formation. Brittle materials are more prone to crack formation owing to lower heat conductivity and resistance to thermal shock. Delamination which means separation of layers occurs due to lack of bonding and residual stress. Distortion is stress-based defect and occurs when the contraction forces are largen then the bonding force of the first printed layer. It may result in the breaking of part [13, 49, 53].

Oxidation may occur when the melt pool is improperly shielded from atmospheric conditions. Chemical reaction with reactive gases such as oxygen changes the chemical composition of the surface and the printing process can be negatively affected. A process under shielding gas or vacuum environment can solve the oxidation problem. In the metal additive manufacturing process, *the alloying element with a lower melting point may be evaporated* due to the high energy density of the beam. This defect causes a change in the chemical composition of the printed part and reduction in performance. The building orientation and thermal gradient during the process affect the degree of the anisotropy of mechanical properties in the fabricated part. Geometrical defects such as *shrinkage, warpage,* and *delamination* are always a challenge in additive manufacturing. The volume changing during the solidification, temperature gradient, residual stress, and feedstock material characteristics are the main factors of the geometrical defects [13, 16, 54].

7 Post-processing

According to today's technology, most of the metal additive manufacturing technologies require post processing to enhance component's properties and overcome current AM limitations right after the fully part fabrication. The main aims of the post-processing are improving surface quality, dimensional accuracy, mechanical properties, and support structure removal [3, 55].

7.1 Support Structure Removal

Support structure removal is the most common type of post-processing. During the metal additive manufacturing process, many parts need a support structure and this support structure needs to be removed. *CNC machining* and *Wire-EDM* are used for the remove support structure of metal printed parts [3].

7.2 Surface Quality

The surface texture of the fabricated part may be modified for performance or aesthetic reasons. Stair-steps, contour filling patterns, and powder accumulation are common surface textures. During the support structure removal, some marks can also remain on the surface. *Bead blasting* is a common method for a matte surface finish, in which glass beads are sprayed over the part surface to remove marks. Dry or wet *sanding* and *polishing* can be performed for a smooth surface. *Tumbling* can be automatically applied to get a smooth surface. *Dyeing* the part is one of the most common methods based on dipping the part into the bath of dye to infiltrate the components. It gives the part a smoother surface and a uniform color [9, 56].

7.3 Dimensional Accuracy

Functional components may need a high precision that can be achieved by subtractive post-processing such as mechanical, chemical, or electrical machining. Different machine strategies for improving dimensional accuracy are listed in Fig. 8 [56].

Grinding is the most common abrasive machining that can be applied to the AM fabricated part for high surface quality and dimensional accuracy. *Turning* or *milling* can be used if material removal is needed to increase dimensional accuracy. *Drilling* is preferable for fixing the poor circularity of holes. *Laser machining, plasma arc machining,* and *electron beam machining* are some of the thermal-based advanced

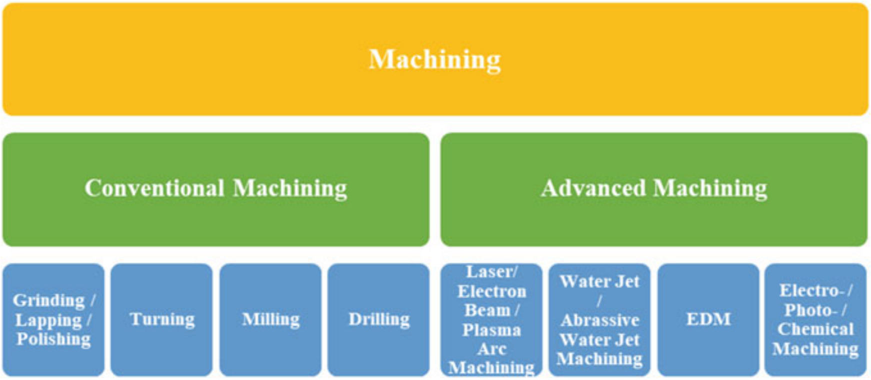


Fig. 8 Different machining strategies for metal AM post-processing

machining methods for removing material from the surface. Chemical processes help to improve surface integrity and dimensional accuracy. *Wire-EDM* is commonly used to remove metal fabricated parts from the build plate. There is no mechanical force, and the accuracy of the cut depends on the diameter of the wire used. EDM can only be applicable to conductive materials [3, 57, 58].

7.4 Mechanical Properties

Successive heating and cooling cycles during the process cause high residual stress on the surface. *Shot peening* is one of the processes that can be performed to take advantage of beneficial residual compressive stress to give resistance to stress corrosion cracking and fatigue failures. The part surface is bombarded with spherical peenings that have a greater hardness than the fabricated part material. Shot peening also improves surface integrity. Turbine blades and gears fabricated by metal AM processes are common applications of shot peening. *Cold Isostatic Pressing (CIP)* is another method to improve mechanical properties, applied under 1000–4000 bar pressure up to 90 °C. CIP is an ideal method for complex geometries. CIP is cheaper than Hot Isostatic Press (HIP), but weaker mechanical properties can be obtained. Therefore, HIP is applied after CIP [3, 56].

After metal additive manufacturing such as DED and PBF, heat treatment is performed to relieve residual stress and to gain desired microstructures. Heat treatment can also improve mechanical properties such as hardness, ductility, wear resistance, and fatigue life. Annealing, homogenization, and recrystallization are generally performed to achieve desired microstructure and uniform properties. *Hot Isostatic Process (HIP)* is one of the common heat treatment processes applied to additively manufactured metal parts. The process is a combination of high heat and pressure. The process is generally applied under 100 MPa pressure around 1000 °C for 2–4 h to decrease the level of porosity, relieve the residual stress and enhance the fatigue life. It is the most suitable heat treatment for the components used in the aerospace, automotive, and biomedical industries [8, 16].

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Chapter 5
Biomaterial Based Additive Manufacturing

Chen Jiao, Lida Shen, and Changjiang Wang

Abstract Additive manufacturing (AM) has been applied to the field of medical engineering since its beginning. It takes into account individual differences and tailors treatment to patients. At present, the design and additive manufacturing of personalized medical implants and prostheses has become the optimal approach, and it has proved to be a reliable solution for many patients who require prosthesis implantation. Many metallic, ceramic and polymeric materials can be used for medical implants. These biomaterials need to have good cell compatibility, without toxic ion release and with similar mechanical properties to human tissues, as well as a suitable degradation rate. However, obtaining an ideal material for tissue engineering via material design is still a problem to be overcome. In this chapter, different types of biomaterials as well as their modification methods are introduced. In addition, recent advances in biomaterial based additive manufacturing are covered, for example, designing an ideal structure which can not only bear loads or stresses but also transfer nutrients required for cell differentiation. More and more biological applications will certainly emerge in the future with the advancement of additive manufacturing technology and biomaterials.

Keywords Additive manufacturing · Biomaterials

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1 Ceramic Biomaterials for Additive Manufacturing

The National Institutes of Health Consensus Development Conference of the USA defines biomaterial as any substance (other than drugs) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats or replaces any tissue, organ, or function of the body. Therefore, biomaterials are distinct from other classes of materials because of the special requirement of meeting biocompatibility criteria.

In tissue engineering, there has been an increasing emphasis on multifunctional implant materials. Bioceramics are artificial bone repair materials that have similar composition and strength to human bones. Bioceramics are also non-toxic to humans and can be used in artificial joints, dental implants, and bone filling material, as can be seen in Fig. 1. According to the chemical properties of the materials, bioceramics can be divided into bioinert ceramics and bioactive ceramics.

1.1 Bioinert Ceramic Biomaterials

The typical bioinert ceramics include alumina and zirconia. This kind of material has superior wear resistance, high compressive strength, good corrosion resistance and is non-toxic to human tissues. It can be used as a total hip replacement implant and fracture fixation device. At the same time, this kind of material shows good colour and transmittance properties after grinding and has been widely used as oral implants in recent years. However, along with excellent mechanical properties, inert ceramics have poor fracture toughness, which causes difficulty in processing and the risk of brittle fracture after implantation.

Fig. 1 Inert ceramic hip joint implants

1.2 Bioactive Ceramic Biomaterials

Bioactive ceramics can gradually integrate with tissues over time after implantation, which is an important feature different from inert ceramics. Bioactive ceramics are mainly divided into calcium-phosphorus based biomaterials and calcium-silicon based biomaterials. The main properties of bioceramics are compared with those of human bones, as shown in Table 1.

The most representative calcium-phosphate-based bioceramic is hydroxyapatite (HA), an important inorganic component of human bones. When it is used in an implant, the surface and pores of HA can be attached to bone tissues, and the binding strength of HA can even exceed the strength of the implant itself or surrounding bone tissues. Although calcium-phosphorus bioceramics have higher stability than other biological materials, they have the disadvantage of a low degradation rate. In addition, compared with natural bone, the artificial HA material lacks zinc (Zn), silicon (Si), strontium (Sr) and other trace elements, which is different from the natural bone in terms of comprehensive performance. Some researchers proposed to prepare biphase calcium phosphate (BCP) with HA as the main component to obtain better bone-inducing ability, which has been verified in animal experiments. Some researchers have also tried to use trace element modification to obtain the ideal effect.

Calcium-silica-based bioceramics are derived from bioactive glass. At present, typical calcium-silica-based bioceramics include calcium silicate ($CaSiO_3$), dicalcium silicate (Ca_2SiO_4), and tricalcium silicate (Ca_3SiO_5). The latter two kinds of calcium-silica-based ceramics are often used in bone cement. The first, calcium silicate, has more stable chemical properties, and is commonly used to prepare porous bone scaffolds. It has been extensively studied. Calcium silicate bioceramics can rapidly induce the deposition of hydroxyapatite on the ceramic surface in body fluids,

Table 1 Mechanical properties of bioceramics compared with human bones, reproduced from [1] by author with permission from John Wiley and Sons

Material	Compressive strength/MPa	Bending strength/MPa	Elastic modulus/ MPa	Fracture toughness/ $MPa \cdot m^{1/2}$
Human cortical bones	100~230	50~150	7~30	2~12
Human cancellous bone	2~20	1.5~38	0.1~0.5	1.0~1.4
Hydroxyapatite, HA	500~1000	115~200	75~103	0.7~1.3
Tricalcium phosphate, TCP	460~680	140~154	33~90	–
Bioglass, CaO&SiO_2	350~500	180~200	100~120	1.9
Calcium silicate, $CaSiO_3$	–	294	46.5	2.0

and its promotion effect on cell proliferation in the short term is better than that of calcium-phosphorus bioceramics. However, the degradation rate of calcium silicate ceramics is too fast to match the growth rate of new bone tissues, and the dissolution of silicon ions causes the pH value around the implant to rise, which has a certain inhibitory effect on cell proliferation.

1.3 Functionalization of Ceramic Biomaterials

To functionalize bioceramic materials, a feasible approach is to add specific inorganic ions contained in human bones to promote the formation of new bones, stabilize bone structures, and promote the proliferation and differentiation of osteoblasts. In fact, the crystal structure and properties of bioceramics can be changed by adding functional elements such as magnesium (Mg), strontium (Sr), zinc (Zn), copper (Cu), silver (Ag), calcium (Ca) and cobalt (Co). Mg, for example, is an essential element in the human body, lack of which is closely related to osteoporosis and other symptoms. Mg is also involved in metabolism in the body, stimulates cell growth and proliferation, promotes bone mineralization, and has certain antibacterial effects, as seen in Fig. 2. It has been proved that Mg-modified HA can significantly improve the antibacterial properties and is effective in the formation of osteoblasts and blood vessels. As for Mg modified wollastonite ($Ca_3Si_3O_9$), significant new bone growth has been observed in the 4th week of implantation. At the same time, Mg concentration decreases gradually during bone reconstruction and tends to disappear in mature tissues, thus not causing damage to the human body due to excessive Mg concentration.

In another example, Sr has been proven to promote the osteogenic differentiation of mesenchymal stem cells, which play an important role in improving bone strength and promoting the biological activity of bone cells. Sr can replace Ca in the HA lattice, and suitable content of Sr can cause defects in the apatite crystal structure, thus improving its dissolution rate and changing its physical and chemical properties in biomedical applications. The use of Sr-modified HA scaffolds to promote bone regeneration and binding can currently reach the level of strontium ranelate and can be used as a safe alternative for the treatment of osteoporotic bone defects.

Zn can induce bone formation by stimulating protein synthesis and enhancing ATP activity in osteoblasts. Zn deficiency is an important cause of decreased bone density and slow bone growth. Cu is an important element that plays the function of the human enzyme. In bone tissue culture, it can promote angiogenesis by stimulating endothelial cell proliferation, and the released ions can also promote the killing of bacteria, thus achieving antibacterial properties. By modifying biphasic calcium phosphate with Cu, it was found that the solubility of biphasic calcium phosphate was improved. Other modifying elements include Ag, Ca, and Co, and the functions of each element are shown in Table 2.

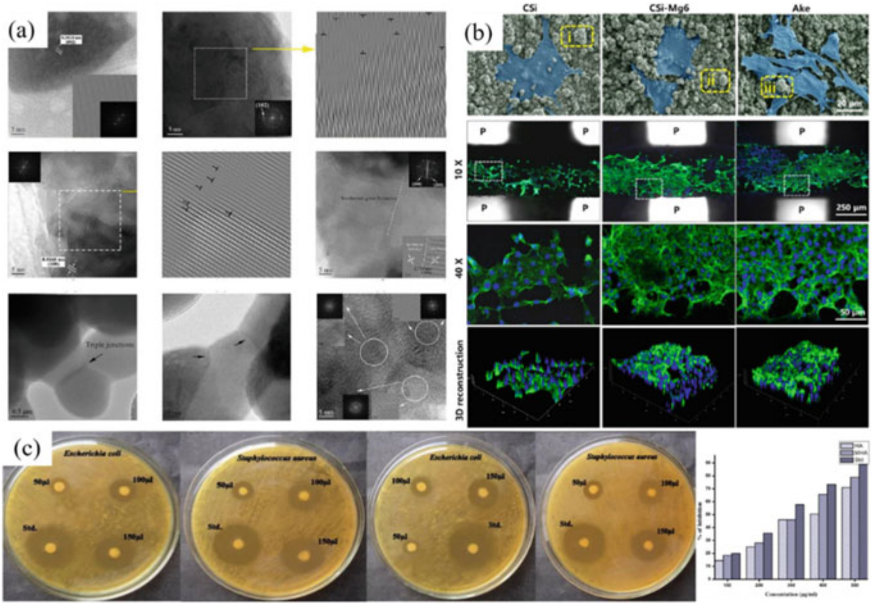


Fig. 2 Bioceramic materials modified by functional elements [2, 3] **a** Dislocation and distortion caused by doping functional elements. **b** Promotion of cell growth, reproduced from [2] by author with permission from Elsevier. **c** The modified materials have similar effects with antibacterial drugs, reproduced from [3] by author with permission from Elsevier

Table 2 Ions and functions for bioceramics

Ions	Mg^{2+}	Sr^{2+}	Zn^{2+}	Cu^{2+}	Ag^{+}	Ca^{2+}	Co^{2+}
Proliferation of cells	√	√	√	–	–	√	√
Mineralization of cells	√	√	–	–	–	√	–
Inhibition of bone resorption	–	√	√	√	–	√	–
Antibacterial properties	√	–	√	√	√	–	–
Induction angiogenesis	√	√	–	√	–	√	√

1.4 Coatings of Ceramic Biomaterials

Another effective measure of functionalization is the preparation of coatings on the bioceramics. It is well known that ceramic materials themselves are highly brittle, which limits their application in bone restoration surgery. In addition, postoperative infection is also a major cause of the failure of the vast majority of bone repair operations. Fortunately, these problems can be solved by modifying the ceramic surface. The design of these coatings must satisfy several important criteria. Firstly, the coating must be biocompatible and must not trigger significant immune or foreign-body response. Secondly, it must be "osteoconductive" in its promotion of osteoblasts to adhere to, proliferate and grow on the surface of the implant to form a secure bone-implant bonding. Thirdly, the coating should also have certain pores therefore not to block the pores of the matrix. Finally, the coating must have sufficient mechanical stability under physiological stresses associated with patient movement so that it does not detach from the implant surface.

Polymer coating (and infiltration) can be achieved by simply impregnating a highly porous scaffold with the polymer dissolved in an organic solvent or water. So far, ceramic surface coating materials are mainly divided into two categories, synthetic polymer and natural polymer. In most cases, the polymer used is synthetic, including polycaprolactone (PCL), polylactic acid (PLA), poly-DL-lactide (PDLLA), polylactic-co-glycolic acid (PLGA) and polysebacylglyceride (PGS). Natural polymers mainly include silk, alginate, collagen and chitosan. As for the shortcomings of bioceramic bone scaffolders, the coating can play a toughening, drug delivery/antibacterial role.

To demonstrate the toughening effect, the mechanism of natural bone destruction needs to be considered. Natural bone is made of hydroxyapatite and collagen. Collagen fibres play an important role in crack bridging, crack deflection and collagen binding, which greatly improve the toughness of bone. Polymer-coated, as well as polymer-infiltrated inorganic scaffolds, are intended to mimic the composite structure of bone. Under the influence of mechanical loads, the polymer bridges any cracks that develop in the inorganic scaffold, thus improving the overall toughness of the scaffold. As listed in Table 3, polymer coatings have been widely used to toughen ceramics.

The addition of polymer coatings to ceramic scaffolds also offers the opportunity to use them as drug carriers. To date, a range of different drugs has been included in such scaffolds, including antibiotics, non-steroidal anti-inflammatory drugs (such as ibuprofen), and drugs for the treatment of bone diseases such as osteomyelitis or osteoarticular tuberculosis, as shown in Table 4. Wound infection is an extremely serious problem in bone repair surgery. If the drug is released too quickly, the entire drug amount could be released before the infection is stopped. On the other hand, delayed release of the drug will make it difficult to manage the healing of the wound. In this regard, the combination of bioceramics and biodegradable polymers can not only improve the degradability of inorganic materials and change their mechanical/physical properties, but also provide a greater degree of control over the drug release compared to single ceramics.

2 Metallic Biomaterials for Additive Manufacturing

Metals and alloys have been widely used as customized prostheses for hard tissue replacement such as total hip replacement, as well as fracture healing aids such as bone plate, as seen in Fig. 3. Surgical stainless steel (316L), cobalt-chromium (CoCr) alloys and titanium (Ti) alloys are the most commonly used metals for biomedical applications, and their mechanical properties are listed in Table 5. Recently, some

Table 3 Functions of polymer coatings on ceramic scaffolds [4]

Coating	Scaffold	Functions
PCL	β-TCP	Compared with the uncoated bracket, the strength is increased by two times and the toughness is increased by five times
PCL/BG	β-TCP	The compressive modulus and biological activity were further improved
PCL/PLA	β-TCP	The compressive strength is increased by 3–6 times
PCL/silk	BCP	The compressive strength increased by 5 times, and cell proliferation ability increased by about 1.6 times
P(3H8)	HA	The compressive strength increased from 0.11 M to 1.55 MPa
PLGA	β-TCP	The energy required to fracture is 10 times that of a pure scaffold
PLLA	HA	The mechanical strength is increased by a factor of 20
PDLLA	CS	The compressive strength is increased to 1.4Mpa, and the elastic modulus is as high as 50 MPa
PGS	BG	The compressive strength after the coating is 0.4−1 MPa
Silk	BCP	The compression strength is increased by 6 times and the toughness of the support is increased by 12 times
Gelatine	HA	The mechanical properties were significantly improved and bone integration was promoted
Alginate	β-TCP	The mechanical properties are improved and similar to natural bone
Alginate/chitosan	BG	The compressive strength is 4 times that of a pure bracket

Table 4 Drug release of ceramic scaffolds coated with polymers [5, 6]

Drug	Polymer	Scaffold	Results
Tetracycline	HA/PCL	HA	40–60% of the antibiotic was released after 7 days in PBS solution
Vancomycin	PLC	HA	Hard tissue regeneration and wound healing, the release of bioactive molecules
Gentamicin	PLGA	HA	Continuously released drugs according to the degradation rate of the coating
Gatifloxacin	PCL	β-TCP	Sustainable drug release over 28 days

metallic alloys have shown degradation properties after implantation, and so such bioactive alloys have become the research focus in recent years.

2.1 *Stainless Steel*

Stainless steel (316L) was the earliest material used in orthopaedic implants because of its good mechanical strength, low price, excellent machinability and acceptable

Fig. 3 Applications of metallic biomaterials

Table 5 Mechanical properties of metallic biomaterials

	316L	CoCr	Ti	Ta
Density (g/cm^3)	7.9~8.1	8.3~9.2	4.3~4.5	16.65
Elastic modulus (GPa)	189~205	210~253	46~115	186~191
Critical strength (MPa)	540~1000	900~1540	240~1000	170~520
Fracture toughness (MPam$^{1/2}$)	50~200	<100	55~115	/
Elongation (%)	10~40	8~28	6~26	2~30
Wear resistance	★☆	★★★	★	★☆
Corrosion resistance	★☆	★★☆	★★☆	★★★
Biocompatibility	★	★☆	★★☆	★★★

biocompatibility. However, poor wear resistance, corrosion resistance, fatigue resistance and the potential risk of releasing toxic ions such as nickel (Ni), cobalt (Co) and chromium (Cr) have resulted in 316L stainless steel being used only as temporary bone implants, such as bone plates and screws [7]. Stainless steel has been used to fabricate 3D printed dental implants using selective laser sintering/melting (SLS/SLM), specifically liquid phase sintering, where a binding polymer is melted by a laser beam (at~1 J·mm^{-3}) and then used to bind the metal particles. Once printing is completed, the scaffold is heat treated to remove the residual polymer, followed by further sintering and infiltration of bronze to produce an implant of sufficient density.

2.2 Cobalt-Chromium Alloy

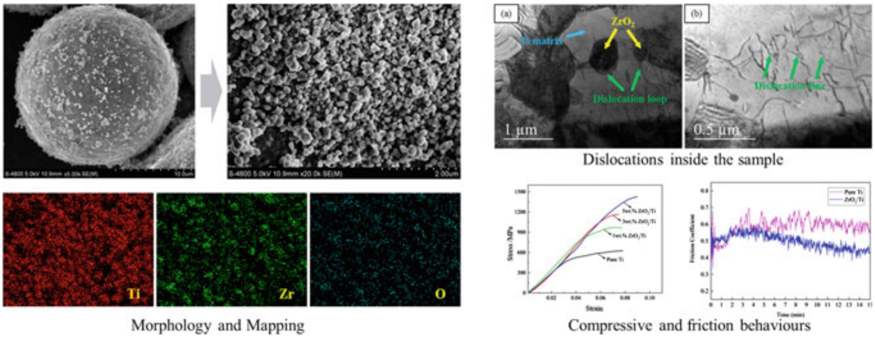
Cobalt-chromium alloy has better mechanical strength, wear resistance, corrosion resistance and fatigue resistance than stainless steel. Even though it has a high price and poor machinability, it is often used in the manufacturing of permanent joint prostheses. Cobalt-chromium implants run the risk of releasing toxic ions such as cobalt (Co) and chromium (Cr) that can cause serious damage to the surrounding tissues. According to the existing research, 3D printed cobalt-chromium alloy is fast solidified with solid solution strengthening, so the hardness is higher than that of the cast alloys. At the same time, 3D printed Co-Cr alloy shows better corrosion resistance because of its homogeneous phase. As for the results of cytotoxicity and apoptosis, 3D printed Co-Cr alloy is superior to cast alloys, presenting high clinical application prospects [8].

2.3 Tantalum

Tantalum is a refractory metal (melting point 2996 °C), which has good mechanical strength, excellent corrosion resistance and biocompatibility. The biocompatibility and outstanding corrosion resistance even exist in an acidic environment, due to the stable and native Ta_2O_5 protective film formed on the implant surface but its high price and poor machinability seriously restrict its wide application in the field of bone implants. However, it is often used as the surface coating material of other metal prostheses. In addition, the high elastic modulus of tantalum metal can cause serious stress shielding between the prosthesis and the bone tissues. In additive manufacturing applications, titanium-tantalum alloys containing 50 wt.% of Ti and Ta can be manufactured into implants using laser powder bed fusion (LPBF). Structurally, these alloys are composed of a Ti-Ta matrix with randomly-dispersed pure Ta nanoparticles as well as equiaxed grains of β phase Ti and Ta in random orientations. Compared to commercial pure Ti and Ti-6Al-4 V alloy, 3D printed Ti-Ta alloy demonstrates higher strength to modulus ratio.

2.4 Titanium and Its Alloys

Titanium based materials not only have lower elastic moduli but also have higher specific strength, better biocompatibility and corrosion resistance while maintaining better fatigue strength. After years of development, titanium has become the most widely used metal implant material in orthopaedic applications. Generally, Al, Sn, V, Fe, Mo, Mn, Cu, Cr, Zr, Ta, Nb and other alloying elements which affect the phase transition temperature are added to Ti to improve its mechanical properties, and


Morphology and Mapping

Dislocations inside the sample

Compressive and friction behaviours

Fig. 4 Toughening effect of zirconia on titanium, reproduced from [9] by author with permission from IOP publishing

form titanium alloys with different microstructure types (α, α+β, β) to meet different application requirements.

Although a variety of Ti alloys have been developed, there are still many common problems. As long-term implants, especially joint prostheses, poor wear resistance of Ti-based materials will produce inflammation, causing debris and structural wear resulting in loss of function. Appropriate surface modification methods such as nitriding and plasma spraying to form high hardness coatings on the surface of the implants can improve these problems to some extent.

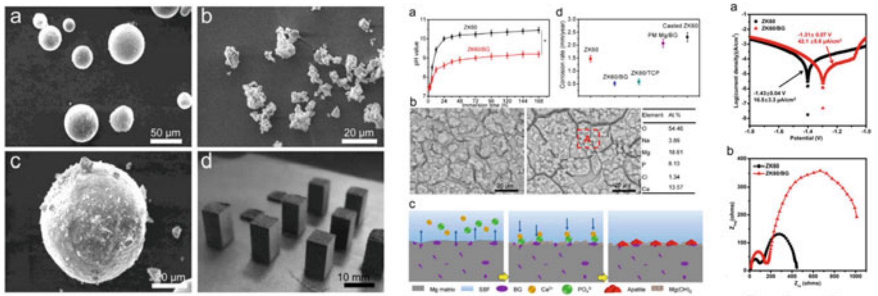
Another method to toughen the titanium is the addition of particles such as zirconia (ZrO_2) and titanium carbide (TiC). Figure 4 shows the Ti particles are uniformly wrapped by zirconia. Zirconia has a uniform distribution in the prepared scaffolds, where the dislocation loops are observed around the zirconia. According to the Orowan mechanism, the dislocation motion not only overcomes the resistance of the zirconia particles but also overcomes the reverse stress of the dislocation loop to the dislocation source. This increases the flow stress, and the hardness of the zirconia doped Ti is almost double that of pure Ti.

2.5 *Magnesium and Its Alloys*

Another type of metallic biomaterial is biodegradable metals including magnesium (Mg), zinc (Zn) and iron (Fe) owing to their good in vivo biocompatibility, controlled degradation rate and sufficient mechanical strength. Compared with degradable polymers, though the degradation cycle may be long, the by-products will not lead to inflammatory tissue response and necrosis.

Mg and its alloys exhibit a similar elastic modulus to that of human bone, which can reduce stress shielding during load transfer at the bone-implant interface. Its density is ~1.79 g/cm^3, which is very close to that of human bone (1.75 g/cm^3). Apart from the favourable mechanical properties, Mg and its alloys are able to completely degrade in vivo, showing an attractive degradation characteristic. It is expected that Mg bone implants not only provide stable mechanical support at the early stage of implantation but also gradually degrade with the restoration of defective bone tissue, perfectly achieving their clinical purpose as temporary substitutes. More importantly, the degradation product, mainly Mg ions, shows no obvious toxicity to human tissues. In fact, Mg is the fourth most prevalent mineral in the human body and acts as an essential element in the construction of bones and soft tissues. A large number of basic studies with encouraging achievements have confirmed the huge potential of Mg alloys as a new generation of bone implant materials. Despite this, there are still several issues that need to be solved before these alloys can fulfil their wide clinical application, including strengthening the mechanical properties and osteoblast proliferation. For example, Mg-Zn-0.5Zr (ZK60) can be used as the matrix, with bioglass (BG) used as the reinforcing particle. A smooth surface and a high densification rate are then obtained via the optimization of printing parameters. The introduced BG promotes the deposition of apatite on the Mg matrix, which not only enhances the corrosion resistance but also improves the bioactivity. Meanwhile, cell tests prove that ZK60/BG exhibits improved cell growth and differentiation as compared with ZK60.

Further research has shown that the porous BG particles have a better promotion effect on the deposition of apatite. Porous BG with a high specific surface area offers a large number of adsorption sites and promotes the in-situ deposition of the apatite layer [10], as shown in Fig. 5. Such a surface film with a relatively stable and dense structure acts as a protection layer, which effectively defends the Mg matrix against aggressive intrusion from the corrosive fluid. The incorporation of porous BG also promote cell proliferation, since it reduces the Mg corrosion and offers a relatively mild environment for cell survival.



Morphology and samples

Formation of apatite layer

Corrosion resistance

Fig. 5 Apatite layer formation of bioglass modified magnesium

2.6 Zinc and Its Alloys

Zinc is another trace element that plays a significant role in the structure and function of proteins, being essential to catalytic functions in more than 300 enzymes. Currently, zinc alloys are being explored for bioresorbable metallic scaffolds, since most tissues have good tolerance to excess Zn ions. Previously, researchers have confirmed that Zn alloy has good biocompatibility through in vivo and in vitro experiments. Despite the above advantages of Zn alloy, the fabrication of Zn implants is still a great challenge at present. Zn alloy has poor processability at room temperature because of its hexagonal-close packed configuration, thus resulting in low efficiency and high cost in traditional processing technologies. In terms of additive manufacturing, the low melting and vaporization points and a limited gap between the two make it difficult in the LPBF process of zinc alloys. Therefore, the processing parameters need to be stabilized to achieve high density when zinc alloys are additively manufactured.

Doping with reduced graphene oxide (rGO) is also reported to tailor the microstructure and enhance the mechanical performance when the rGO doped Zn scaffolds are additively manufactured [11]. The homogeneously distributed rGO contributes to the grain refinement and the weakened texture since the rGO is pinned at the grain boundaries and induces equiaxed growth of grains. The rGO-induced grain refinement and the efficient load transfer caused by the huge specific surface area of rGO and the favourable interface bonding are the two primary strengthening factors that improve the mechanical strength of Zn. At the same time, rGO activates more slip systems in the Zn matrix and simultaneously improves the ductility of these composites.

3 Polymeric Biomaterials for Additive Manufacturing

In addition to metal and ceramic materials, degradable polymeric materials are other kinds of biological materials which have been developed over a long period and are widely used. Degradable polymeric materials refer to materials that are gradually degraded into low molecular weight compounds or monomers by hydrolysis and enzymolysis in the organism and are directly discharged from the body or disappear through normal metabolism in the body. At present, biodegradable polymeric materials for biomedical purposes are mainly used as drug, cytokine and gene carriers, and tissue engineering scaffolds. A degradable polymeric material can provide early mechanical support for bone defect repair, avoid secondary surgical removal, reduce patients' pain, and reduce medical costs. It can also be used as a controlled release carrier for bone growth factors such as BMP-2 to improve the bone inductance of the material. Depending on the sources, degradable polymeric materials can be divided into natural materials and synthetic materials.

3.1 Natural Polymer Materials

Natural polymer materials are derived from natural polymer compounds, which have excellent biocompatibility, bioactivity and hydrophilicity. Most of their degradation products are amino acids that can be directly absorbed by the human body. At present, common natural polymer scaffold materials include collagen, gelatin, chitosan, and silk fibroin. Collagen can be obtained from a wide range of sources and can mimic the function of an extracellular matrix, making it a potential candidate for tissue engineering scaffolds. However, due to the inherent flexibility and high biodegradability of collagen, scaffolds made of single collagen may have insufficient mechanical properties after implantation into the defect site and risk the collapse of the scaffold due to rapid degradation. Therefore, it is necessary to compound hydroxyapatite (HA), bioactive glass (BG) and other inorganic materials with collagen to prepare bone scaffolds with good mechanical properties and biocompatibility. Chitosan is another natural polymer with good biocompatibility, biodegradability, minimal immunogenicity and antibacterial properties, which can promote the growth of osteoblasts and mineral matrix deposition. It has been used in skin, nerve, bone and cartilage, and liver tissue engineering, as well as wound dressings and drug sustained-release agents. However, the scaffolds prepared from pure chitosan also have defects such as poor mechanical properties and lack of surface specificity, and so they usually need to be combined with other materials. So far, natural polymer materials have been widely used in the medical field. However, the mechanical strength of almost all pure natural polymer scaffolds is too low and the degradation rate is uncontrollable. In addition, natural polymers also have poor machinability, and it is difficult to prepare personalized shapes and internal porous structures according to the requirements. These factors limit their further application in tissue engineering.

3.2 Synthetic Degradable Materials

Table 6 lists the advantages and disadvantages of some polymeric biomaterials.

The main synthetic degradable materials used in additive manufacturing are aliphatic polyesters, whose main chains are mostly connected by aliphatic structural units through easy hydrolysis ester bonds, which are easily degraded into non-toxic water-soluble oligomers or monomers by a large number of microorganisms in nature or enzymes in animals and plants, and then converted into energy, CO_2 and H_2O by microorganisms. Among them, polylactic acid (PLA), polyglycolicacid (PGA) and PLA/PGA copolymer (PLGA) are the most widely used in orthopaedics [13]. PLA and PGA are the first biodegradable polymeric materials approved by the FDA for clinical use and have been used in clinical applications such as surgical sutures and orthopaedic internal fixation materials. However, the mechanical properties of these materials are still relatively low and they lack the necessary biological activity and cell response ability. Currently, researchers have proposed adding nucleating agents

Table 6 Functions of different polymeric biomaterials [12]

Materials	Advantages	Disadvantages
Collagen	Similar to an extra cellular matrix (ECM), cytocompatibility, enzymatic biodegradability, versatility in being processed in different physical forms, FDA approved	Low mechanical strength, difficulty in disinfection and handling
Gelatin	Cytocompatibility, biodegradability, porosity tenability, osteoconductivity	Poor mechanical properties, low stability in physiological conditions
Silk fibroin	Cytocompatibility, immunogenicity, flexible processability, limited biological adhesion, high mechanical strength, thermal stability, easy chemical modification	
Chitosan	Cytocompatibility, biodegradability, cell-binding, differentiation and migration properties, antibacterial properties, mucoadhesivity	Poor mechanical strength and stability, rapid in vivo degradation rate
Alginate	Cytocompatibility, tuneable properties, easy gelling	Difficulty in sterilization, low cell adhesion
Cellulose	Hydrophilicity, cytocompatibility, bioactivity, optical transparency, tuneable properties	
PCL	Cytocompatibility, biodegradability, slow degradation rate	Hydrophobicity, low bioactivity
PLA	Cytocompatibility, thermal stability, tuneable properties	
PLGA	Wide range of degradation rates, tuneable properties	Suboptimal mechanical properties, poor osteoconductivity

such as nano silica to promote chain nucleation growth and ordered arrangement of poly-L-lactic acid (PLLA) molecules, to improve the crystallinity and strengthen the mechanical strength of the scaffolds. Some researchers have also added carbon-based materials to regulate the behaviour of bone marrow stem cells through physical signals, ultimately enhancing osteogenic differentiation.

4 Applications of Biomaterials Based Additive Manufacturing

With the rapid development of additive manufacturing, its potential application fields are being expanded. Specific to biomedical applications, the unique and significant advantages in high precision, personalized manufacturing and complex shape construction of additive manufacturing are becoming important driving forces for upgrading medical industries. From the perspective of implementation difficulty and

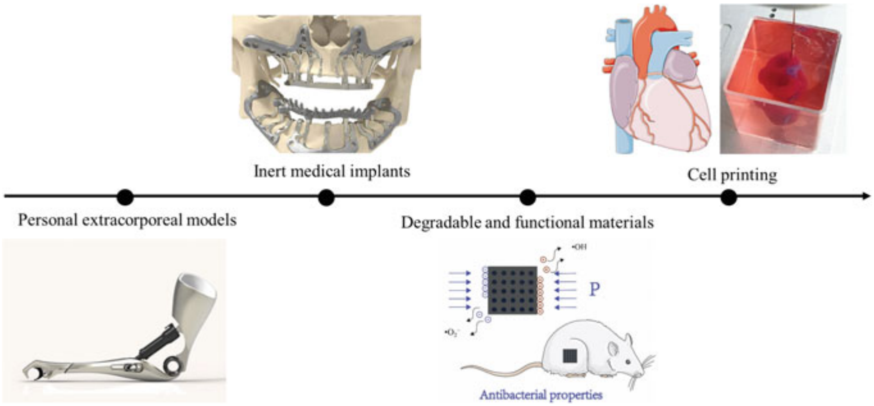


Fig. 6 Four stages of additive manufacturing applications

technology maturity, the applications of additive manufacturing can be divided into four stages as shown in Fig. 6 and as follows:

Stage 1: Manufacturing of personalized extracorporeal models. With the assistance of these models, surgeons can perform more intuitive planning before surgery to improve the success rate. Generally, these models do not possess special features such as biocompatibility. Examples for this stage are wearable prosthetics and other extracorporeal medical devices.

Stage 2: Manufacturing of personalized medical implants. The use of inert materials represented by titanium alloys and PEEK (polyether-ether-ketone) can help support the deficient parts caused by disease or accident. These materials should be biocompatible and non-toxic to human bodies.

Stage 3: Manufacturing of degradable and functional scaffolds for tissue engineering. These scaffolds should be degradable in human bodies with the release of necessary elements and substances. Meanwhile, the cells can proliferate and differentiate on the scaffolds. Thus the design of materials is crucial in this stage.

Stage 4: Manufacturing of tissues or artificial organs via cell printing. Stem cells and an extracellular matrix are distributed in three dimensions with the use of gel or collagen. At present, drug screening is the major target of this stage.

Here, the research on the second and third stages will be presented in detail. A large number of researchers have enriched the application of additive manufacturing in the field of tissue engineering from the perspective of materials and functionalization, and many clinical cases have verified the feasibility of additive manufacturing in this research direction. There are more than three million bone transplant surgeries performed worldwide each year. For a healthy bone skeletal system, bones are in a constant process of remodelling to adjust to mechanical injuries and tiny lesions. However, once the bone defects exceed the critical size that bone can repair by itself, bone substitutes are needed for healing. Since it was difficult to meet the treatment needs with traditional bone substitutes, including autologous bone and allogeneic bone, synthetic materials have gradually become the focus of research. At present,

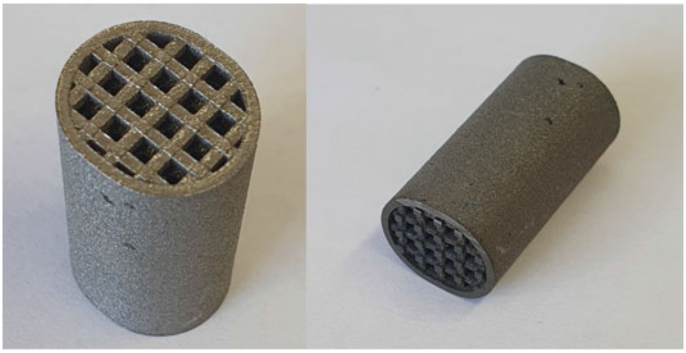


Fig. 7 Porous femoral stem

one example of medical implants made of additive materials that has been clinically applied is lumbar interbody fusion cages The up to 80% porosity structure allows for bony ingrowth and provides a similar modulus of elasticity to cancellous bone which can minimize stress shielding. A porous femoral stem created from additive manufacturing is shown in Fig. 7, it can reduce the stiffness of the implant.

In another application, 3D printed porous bone scaffolds are commonly used in bone defect repair and bone tissue engineering. These scaffolds provide mechanical support to resist external stress, maintain the original shape and integrity of tissues, connect with the surrounding tissues and guide the tissues to grow. Some scaffolds can also release bioactive ions, thereby promoting the physiological behaviour of cells and serving the purpose of treatment [14]. In dental applications, for example, bone substitutes are often obtained from other body parts in traditional maxillofacial reconstruction methods, which will cause secondary injury to the human body. Moreover, the replacement bone, harvested from elsewhere in the body, has a significant difference in shape from the defect site, greatly affecting the aesthetic and later functional recovery. After grafting, maxillofacial bone replacement should meet the essential support and chewing functions and induce bone ingrowth after a certain recovery period. With the application of additive manufacturing, porous bone scaffolds with complex internal structures and highly personalized geometry can be obtained. Test results show that the mandible stress is distributed symmetrically, and the graft of the unilateral prefabricated reconstruction plate and maxillofacial prosthesis effectively balances the stress transfer during the occlusion process. As shown in Fig. 8, the maximum stress on the undamaged mandible appears between the condyle and coracoid, with little difference between the left and right sides. Moreover, the deformation is relatively small, which means it will not destroy the safety and stability of the maxillofacial prosthesis. The proposed method can effectively reduce the surgical trauma and postoperative impact on the defective parts, significantly shorten the operation time, and improve the restoration effect of the teeth.

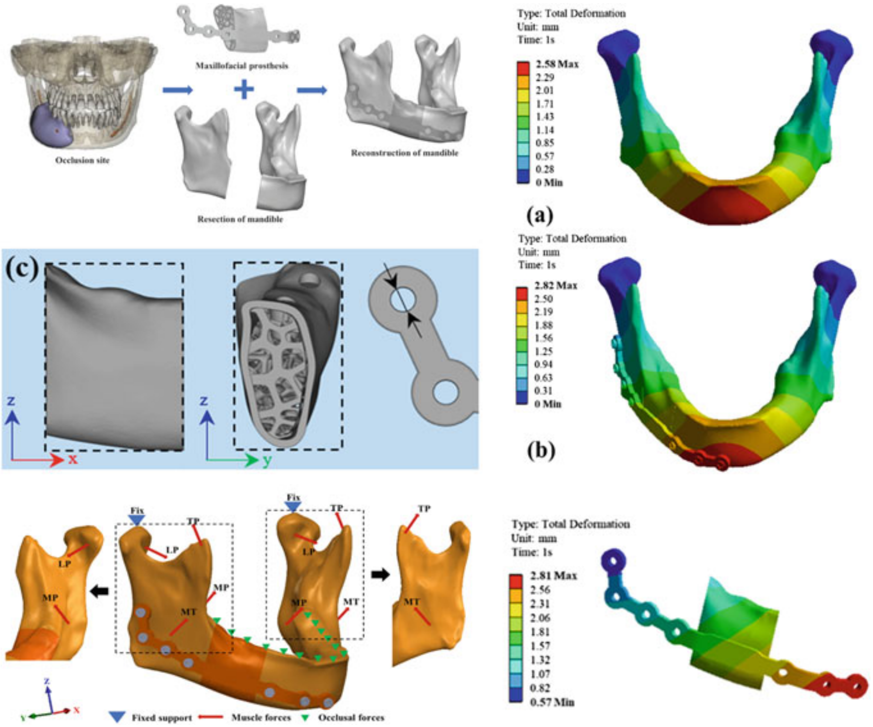


Fig. 8 The mandibular reconstruction process and the deformation of the healthy mandible compared with the mandible implanted with the prosthesis, reproduced from [15] by author with permission from Springer Nature

Porous cartilage scaffolds can also be prepared when natural materials such as collagen and similar gels are used as base materials. Cartilage is a type of hard and elastic tissue located between the bones and containing chondrocytes. The additively manufactured cartilage scaffolds have two functions. On the one hand, the scaffolds are implanted in articular cartilage defects to simulate the highly porous and porous microenvironment in vivo, providing appropriate mechanical support and physical and chemical stimulation for the combination of cells or growth factors. On the other hand, biodegradable scaffolds coated with drugs/cells are injected into the articular cartilage defect, causing less scarring and reducing patients' pain. Based on the layer-by-layer characteristic of additive manufacturing, bone/cartilage tissue engineering scaffolds can also be realized, which not only simulate the multiphase material of natural cartilage tissue but also mimic the complex hierarchy of natural bone/cartilage tissue. Moreover, TGF, IGF, BMP and other active factors have been gradually added by researchers into bioink for biological stimulation, to induce different layers of cells in the scaffold to achieve region-specific differentiation and growth. With the development of biomaterials, bioactive substances with proteins and cells can be printed, and the scope of application has gradually developed from hard tissues like bone to soft tissues like blood vessels and skin. Even organs containing complete structures are also being printed. Some tissues and organs printed with bioink are shown in Fig. 9.

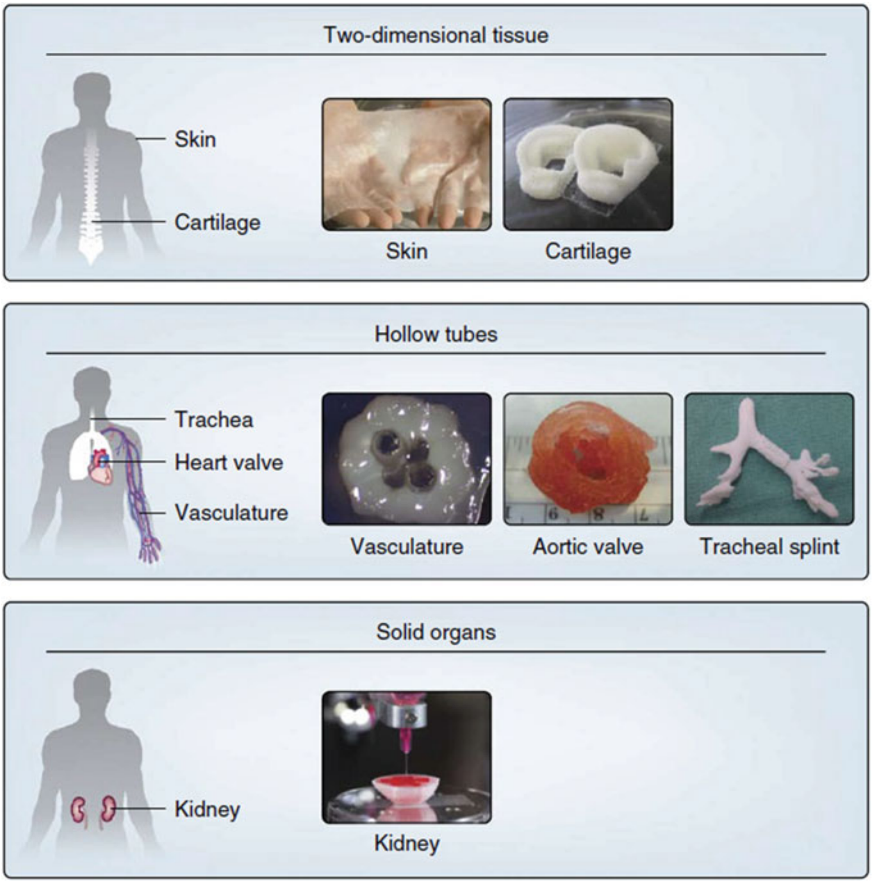


Fig. 9 Tissues and organs printed with bioink, reproduced from [16] by author with permission from Springer Nature

5 Recent Advances in Biomaterial Based Additive Manufacturing

5.1 The Structural Design of Biomaterial Based Additive Manufacturing

In regenerative medicine approaches, porous scaffolds or implants are commonly used for inducing the regeneration of tissues. The material and the structure of the scaffolds are both important factors. Composite materials suitable for bone regeneration were discussed in the previous section, and some innovative structural design methods suitable for tissue engineering will be introduced in this section.

According to recent research, the pore geometry of the porous scaffolds shows a significant effect on the tissue regeneration process, and the structure and the effect of structural changes on parameters such as cell viability are most evident in the early stage. The curvatures of structures were studied, and curvatures with radii much larger than those of the cells could interact with the cells and influence their behaviour. According to quantitative analysis, the rate of tissue generation is proportional to the curvature of the surface. Meanwhile, the cells and tissues tend to attach to and proliferate on concave surfaces rather than convex and flat ones. With the deepening of research, researchers attempted to characterize the three-dimensional characteristics of the scaffold structure with porosity, pore size and pore geometry. The most important finding is that the requirements regarding the pore size are different when comparing in vitro studies with in vivo studies. Generally, pore sizes over 300 μm are recommended for scaffolds. In addition, lower porosity may be beneficial in vitro, because cell proliferation will be controlled and cell aggregation could be forced when the porosity is lower. In comparison, higher porosity and larger pore sizes may be advantageous in vivo, because they could stimulate bone regeneration. The effect of pore geometries on cell adhesion is shown in Fig. 10.

An ideal tissue engineering scaffold should mimic the internal structure of natural bones, with interconnected gradient pore structures, allowing protein adsorption, cell diffusion and effective transport of nutrients, oxygen, growth factors and waste to promote the growth of new tissues inside the scaffold until the scaffold is completely degraded and the new tissues are fully generated to achieve the ultimate goal of repairing the defects. Human bones are porous, especially cancellous bones, and pores are amorphous and mainly play a role in stress transfer. Suitable stress distribution is an important factor to promote the growth of cells and tissues. The design and preparation of bone-like structures have always been a major problem in the field of tissue engineering. At present, additive manufacturing with a high degree of freedom manufacturing capability has greatly promoted the development of porous structures applied in tissue engineering and realized the required design parameters (porosity, pore shape, pore size, etc.).

In the early research of porous scaffolds, standard polyhedrons (such as cubes, spheres, cylinders and hexagons, etc.) were used to construct cells through Boolean

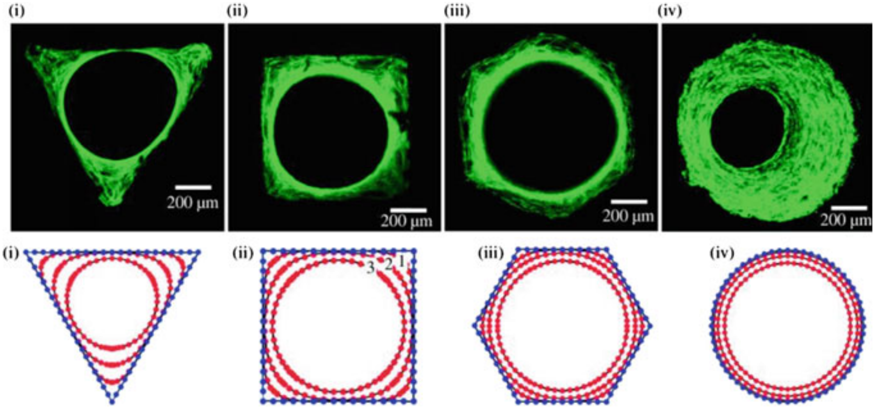
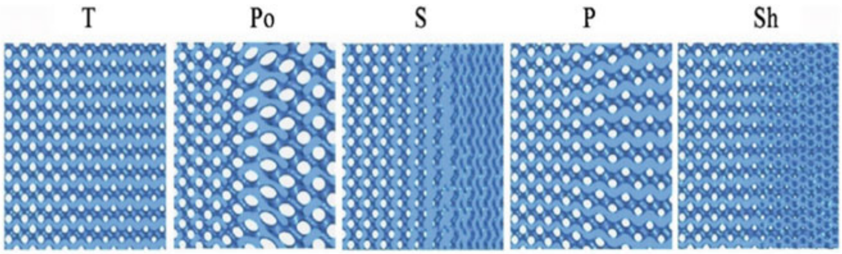


Fig. 10 Effect of pore geometries on cell adhesion, reproduced from [17] by author with permission from The Royal Society

operation and regular array to create 3D models. As an early attempt to design porous scaffolds, this method only carried out simple Boolean operations and arrays, and the parameters such as porosity and gradient porosity of the scaffolds were poorly controlled. The mathematical modelling method was then developed. In it, geometric functions are used to construct the porous structure with implicit function surface or irregular multilateral body. Design using Triply Periodic Minimal Surfaces (TPMS) shows great vitality in the gradient and mixed porous structures among different methods, where both pore size and porosity can be adjusted to obtain a graded structure by properly tuning the parameters of the TPMS equation, as shown in Fig. 11.

According to Zhang et al. [19], a programmable, biomimetic TPMS scaffold with graded pore size for tissue engineering allows the reconstruction and replacement of defective bone with energy-absorbing properties, biocompatibility for cell attachment, and function of angiogenesis, as shown in Fig. 12. Based on the constraints of bone structure parameters, the pore size and performance can be realized by adjusting the parameters of a single-layer structure. The graded scaffold design without stress concentration is realized through the smooth connection between different layers, and the relative density of the scaffold is within the required range of the relative density of bone tissue. Corresponding scaffolds can be selected to provide model and data references for the different design types of bone implants.

Voronoi methods have been recently adopted in tissue engineering. A Voronoi diagram is a partition of a plane into regions close to each of a given set of objects. It could reflect many features in nature, such as clathrus ruber, leaf veins, giraffe fur, and cracked earth. Due to inherent bionic characteristics, this nature-inspired geometric representation method is useful when constructing a trabecular-like structure. It can successfully imitate the structural morphology of cancellous bone by adjusting the distribution of seeds and scaling factors. When constructing such structures, a regular seed set is generated in restrained space. These seeds are subsequently redistributed



Type	TPMS equations
T	$\phi_T = \alpha(x, y, z)(\cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) - 0.85) + (1 - \alpha(x, y, z))(\cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) - 0.3) > 0$
Po	$\phi_{Po} = \cos(K_z(x, y, z)x)\sin(K_z(x, y, z)y) + \cos(K_z(x, y, z)y)\sin(K_z(x, y, z)z) + \cos(K_z(x, y, z)z)\sin(K_z(x, y, z)x) - 0.85 > 0$ $K_z\left(x, y, z\right) = \left(1 - \frac{1}{1+e^{-0.5(x-7.5)}}\right) \times 1.33 + \frac{1}{1+e^{-0.5(x-7.5)}} \times 0.87$
S	$\phi_1 = \cos(a(x - 1.5\alpha(x, y, z)))\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(a(x - 1.5\alpha(x, y, z))) - 0.85 > 0$ $\phi_2 = \cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) - 0.85 > 0$ $\phi_S = \phi_1 \cup \phi_2,$
P	$\phi_P = \cos(ax(1 - 0.23\alpha(x, y, z)))\sin(ay(1 - 0.23\alpha(x, y, z))) + \cos(ay(1 - 0.23\alpha(x, y, z)))\sin(az(1 - 0.23\alpha(x, y, z))) + \cos(az(1 - 0.23\alpha(x, y, z)))\sin(ax(1 - 0.23\alpha(x, y, z))) + 0.55\alpha(x, y, z) - 0.85 > 0$
Sh	$\phi_1 = \alpha(x, y, z)(\cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) + 0.5) + (1 - \alpha(x, y, z))(\cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) - 0.85) > 0$ $\phi_2 = \alpha(x, y, z)(\cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) - 0.73) + (1 - \alpha(x, y, z))(\cos(ax)\sin(ay) + \cos(ay)\sin(az) + \cos(az)\sin(ax) - 1.5) > 0$ $\phi_{Sh} = \phi_1 \setminus \phi_2$

Fig. 11 Construction of TPMS structures, reproduced from [18] by author with permission from Elsevier

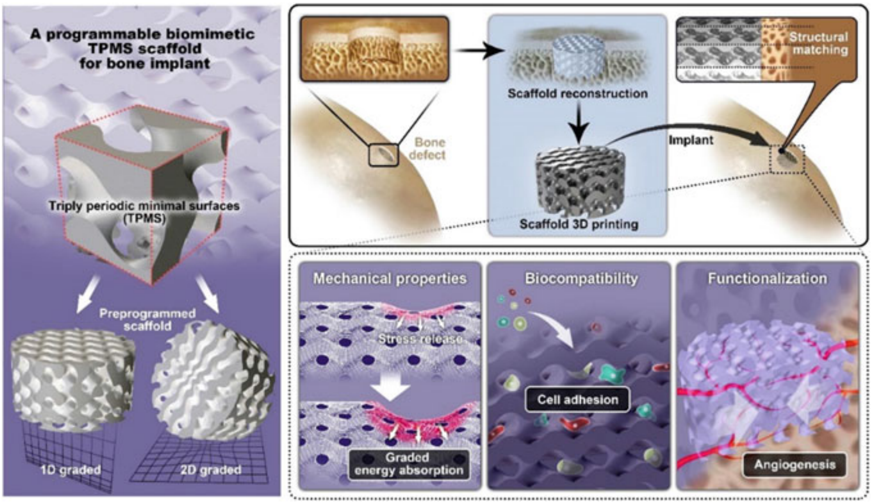


Fig. 12 Functions of TPMS structures, reproduced from [19] by author with permission from Elsevier

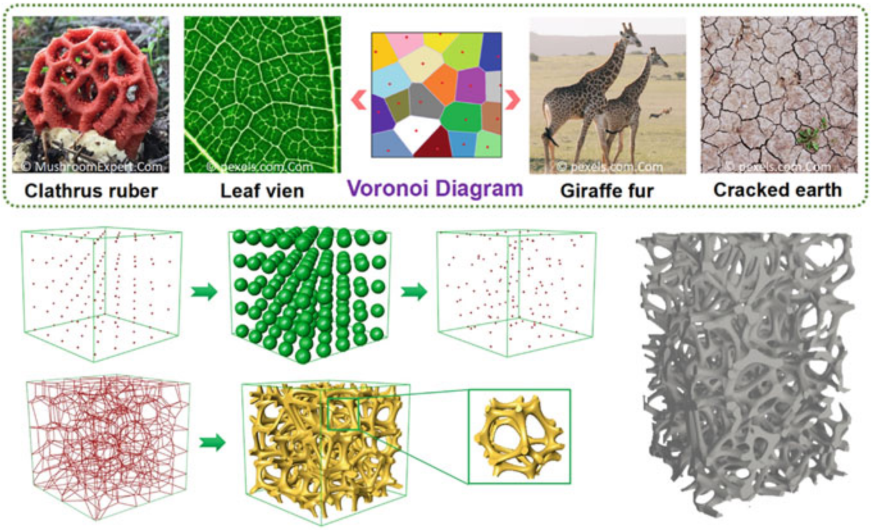


Fig. 13 Construction of Voronoi structures, reproduced from [20] by author with permission from Elsevier

randomly according to a prescribed algorithm. The Voronoi cells are then calculated based on the new seed set, and finally the porous structure is generated. Some Voronoi structures and modelling methods are shown in Fig. 13.

According to the results of in vitro and in vivo experiments, the irregular Voronoi structures possess a stronger ability to induce cell proliferation and differentiation in the middle and late stages of osteogenesis than the regular scaffolds. In addition, osteoid and bone deposition tends to occur in the inner hole surface with large curvature and the places with low local porosity. Also, the trabecular-like scaffold has more even new bone formation in the bone ingrowth direction, without the distribution faults that often occur with a regular scaffold, as shown in Fig. 14. Firstly, the irregular porous Voronoi scaffolds have diversified local porosity and more pores with variable curvature. The pores with large curvature or small size hinder the diffusion of cytokines and growth factors, and provide anchor points for cell adhesion. Secondly, in the middle and late stages of trabecular-like scaffold bone regeneration, its random combination with large and small pores in any direction could provide channels for biological factors diffusion and cell migration, preventing a section perpendicular to the direction of bone ingrowth from being completely blocked.

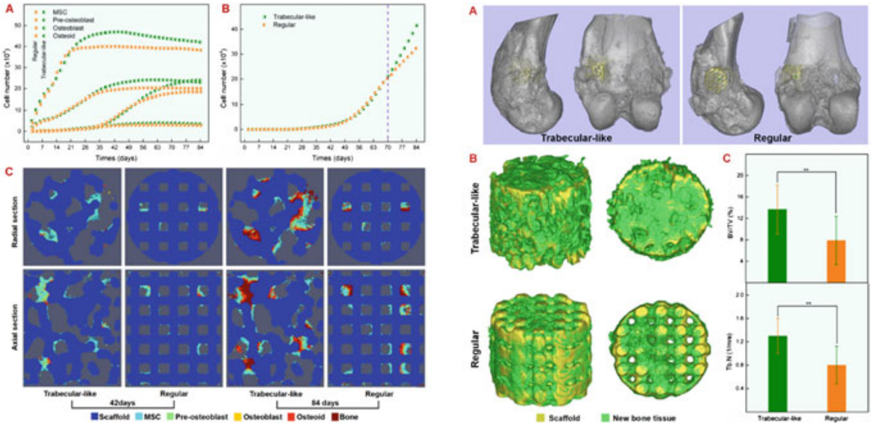


Fig. 14 Function of Voronoi structures, reproduced from [20] by author with permission from Elsevier

5.2 The Deformation Compensation of Biomaterials Based Additive Manufacturing

Porous and conformal structures are preferred in the case of additive manufacturing. Conformal structures can be used as dental movable stents and dental crowns, as shown in Fig. 15. These structures are characterized by thin walls and are easily distorted by the high energy density laser or sintering process in additive manufacturing. Distortion may lower the dimensional accuracy and mechanical properties of the printed parts and may even lead to the interruption of the additive manufacturing process. Therefore, effectively reducing the distortion of 3D printed parts has become a focus of research in recent years.

Pre-distorting the original geometry using distortion data is an effective method to reduce the final distortion of parts, including the actual measurement of distorted geometry by adopting computer tomography (CT) or optical 3D scanning technology. Studies have been conducted to decrease distortion by optimizing additive manufacturing process parameters, but this can only achieve a limited decrease in distortion. Geometry compensation is another approach to decreasing the distortion of parts.

Fig. 15 Dental applications (Credit: Nanjing Chamlion Laser co., ltd.)

However, geometry compensation by direct subtraction of measured deviation, such as the mapping method, may lead to regional overcompensation, resulting in reversed distortion of printed parts. With the continuous development of machine learning, artificial neural networks (ANN) have also been used in the simulation and prediction in additive manufacturing, owing to their strong ability to describe highly nonlinear problems and adaptive learning.

Therefore, a new geometry compensation method combined with a genetic algorithm and backpropagation network is proposed. It is applied in the field of complex thin-walled structures of LPBF-fabricated oral maxillary stents. The established GA-BP model belongs to the multi-layer perceptron (MLP) structure. Optically measured distorted geometry coordinates are used as input and original geometry coordinates are used as output for the training of the GA-BP model. After that, the original geometry coordinates are used as input for the trained GA-BP model, to obtain the desired compensated coordinate sets by predicting. The obtained coordinate sets are then converted into point clouds and reconstructed to complete the intelligent geometric compensation of the stent. The final average distortion of the compensated oral maxillary stent is reduced by 71% through this combined geometry compensation method. A more comfortable treatment experience for patients can then be realized through the use of maxillofacial stents that fit extremely well.

6 Challenges and Future Trends

Plenty of attempts have been made to prepare ideal tissue and organ models with the assistance of additive manufacturing, and satisfactory results have been achieved in both in vivo and in vitro experiments. However, some aspects still need to be focused on and improved. It is expected that more and more biological applications of additive manufacturing will emerge in the future such as exploring 3D printing of silver antibacterial bone scaffolds [21].

6.1 Gradient Structures with Macro and Micropores

According to relevant research, pore size is a major determinant of the mechanical properties and biocompatibility of tissue engineering scaffolds [22, 23]. Gradient structures are also important. For example, Hazlehurst et al. [24] investigated the functionally graded cobalt chrome femoral stem manufactured using a selective laser sintering process. Pores of different sizes have different functions in bone implants. A pore size of $0.1-1$ μm can improve the surface roughness and specific surface area of the scaffolds, thereby increasing the cell adhesion and promoting the exchange of body fluids. A pore size of 40–100 μm allows the growth of non-mineralized tissues. If the pore size is increased to 150–200 μm, the growth of osteoblasts will be better. Macro pores with a pore size of more than 300 μm can regulate the mechanical properties of scaffolds, make them more compatible with human tissues, and enhance the formation and inward growth of capillaries. Gradient structures that combine macro and micropores are closer to human tissues in terms of function. In the process of additive manufacturing, macro pores are more concerned, micro pores could be made through the addition of functional materials. For example, materials that can be pyrolysed or volatilized are added, through additional processes right after the additive manufacturing process, the interconnected pores can be obtained.

6.2 Biomaterials with Magnetic and Dielectric Properties

Scaffold-guided regeneration plays a crucial role in the treatment and repair of severe defects caused by trauma, tumour and excision. Currently, magnetic functional scaffolds combined with external magnetic fields have been proven to affect cell metabolic behaviour and promote bone tissue regeneration through the magnetic environment. The external magnetic fields can also drive drug-loaded magnetic particles, effectively regulating drug release and activating cell surface channels, so that growth factors, hormones, peptides and other factors can be directionally deposited on scaffold tissues to form a series of osteoblast-related pathways, and finally promote tissue growth and defect regeneration. Magnetic scaffolds also have extensive application potential in the fields of hyperthermia, magnetic resonance imaging, and targeted delivery. Therefore, magnetic materials can be used to improve the efficiency of bone tissue engineering and provide a certain guarantee for the repair of defects. At present, magnetic scaffolds are attracting more and more researchers' attention. Similarly, it has been found that when human tissue is subjected to force, the electrical dipoles in its collagen are deflected, resulting in a negative charge on the surface, creating an electric potential that provides electrical signals to cells. Therefore, biological materials with dielectric properties are used to create an electric field in situ to stimulate bone tissue regeneration. Based on this idea, the use of electrical stimulation to repair bone defects has become a research hotspot.

6.3 Vascularization of Tissue Engineering Scaffolds

Research has shown that the key factor affecting the difficulty in the repair of large area defects is an insufficient blood supply to specific anatomical sites. Therefore, the vascularization of tissue engineering scaffolds is the basis to ensure the survival of grafts, and also the key technology in bone tissue engineering. The seed cells located at the edge of the scaffold can obtain nutrients and oxygen from the surrounding environment through osmosis, but the seed cells located 200 μm inside the scaffolds can only obtain the required substances through the reconstruction of the blood transport system. Therefore, in bone tissue engineering, graft vascularization is an important basis for bone defect repair, and the degree of vascularization is positively correlated with the number of new bone formations. At present, the commonly used method is to combine the culture of vascular endothelial cells and seed cells to form a matrix with scaffold materials, which can be implanted in vivo to promote angiogenesis and promote the growth and differentiation of seed cells through the mutual regulation between cells. Another method is to use growth factors to promote the formation of blood vessels through the combination of the growth factors with the scaffold material. Therefore, the vascularization of additively manufactured scaffolds is a crucial problem to be addressed.

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Chapter 6
Composite Based Additive Manufacturing

Sk Md Alimuzzaman and Muhammad P. Jahan

Abstract Additive manufacturing (AM) has become an extremely popular manufacturing process due to the immense potential it holds for the development of new products and applications across a wide range of industries. Due to its capacity to produce complicated geometries with little to no waste, it is frequently employed in fast prototyping processes. The growing popularity of polymer composite-based additive manufacturing is due to its versatility for printing with various reinforcements at a relatively lower overall melting temperature, as well as its extrudability and adhesive properties in 3D printed parts. This chapter has briefly covered a variety of 3D printing methods for polymer-based additive manufacturing by discussing the working principles of each AM process. With the input of some recent papers on polymer composite based AM, several reinforcing strategies have been presented along with their improvement on mechanical properties of AM polymer composites. The effects of 3D printing parameters on the composite mechanical properties and the selection methods of printing parameters for improved product performance of AM Polymer composites have been discussed. The internal porosity contributing to the poor strength, and poor dimensional accuracy and surface roughness of 3D printed parts are found to be the two major drawbacks of AM polymer composites. Therefore, the effectiveness of several frequently used post-processing methods on the defect reduction and properties enhancement of AM polymer composites have been reviewed. Finally, a brief discussion on future research scope on the area of AM polymer composites has been added in the chapter.

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1 Introduction

Composites are a group of materials constructed from two or more materials mixed in a specific way which creates a combination where each material is unique and distinguishable. The goal of making composites is to design a new material with the benefits of both materials' strengths while often masking the flaws of the original materials [1]. Selection of fibers plays an important role in composite design, which combines with the polymer and provides the composite material with good mechanical and thermal properties that cannot be achieved on solo possessions. Before the advent of additive manufacturing, polymer processing techniques such as compression molding, injection molding (IM), plastic forming and joining had been frequently used to manufacture composite parts. Major concerns of conventional manufacturing techniques are the limitation of manufacturing complex geometries, higher initial establishment cost, material wastage, and different types of tooling requirement etc. In addition, additional processes, such as computer numeric controlled (CNC) machining is required to obtain the final part from the laminated composites obtained by traditional composite manufacturing processes.

Polymer composite manufacturing has been improved by additive manufacturing (AM), which enables the fabrication of complicated geometries with more design flexibility and shorter lead times. Figure 1 shows some examples of additively manufactured part by polymer composites. Comparing additively made polymer composites to traditional polymer composites, there are several benefits. Complex microstructures and geometries that are not attainable with traditional composite production procedures can be produced with additive manufacturing. This enables the development of materials that can be customized for specific applications and have superior mechanical, thermal, and electrical characteristics. Since additive manufacturing only utilizes the material needed to create a product, it is a "green" approach that generates little waste. This contrasts with conventional composite production methods, which can produce considerable amounts of scrap material. Complex forms and interior features can be produced with the use of additive manufacturing, which is not achievable with traditional production procedures. Designers may now produce components with better functionality and performance with the aid of this. With the quick and simple production of parts made possible by additive manufacturing, designers can readily prototype and try out new ideas which lead to faster development periods and lower costs associated. Particularly for small production runs, additive manufacturing can be more economical than traditional composite manufacturing procedures. This is due to the expense of tooling being eliminated that helps lower the cost of making complicated parts.

In order to avoid inconveniences with traditional composite manufacturing techniques, additive manufacturing, more specifically FDM (Fused Deposition Modelling) has been in use in the small-scale composite manufacturing industries which started using thermo-setting plastics (TSP) and thermo-plastics (TP) for composites. As TPs are recyclable, biodegradable, and stay neutral to nature. The

Fig. 1 Example of objects with composite-based additive manufacturing [3] (***Open Access***)

low cost and less absorbability to moisture make TPs a choice of additive manufacturing materials over TSPs [2]. In addition to this, composites are made with different reinforcements to improve the overall properties of composites. The type of fiber, fiber treatment, fiber size, fiber loading, and fiber properties should all be considered when using fibers in the AM process. Polymer based composites are reputed for their higher specific strength, that is why these composites are becoming increasingly popular in high performance industries like automobiles, sports, structural constructions etc. Fiber reinforced polymer composite in additive manufacturing (AM) is now a challenging area where many researchers are working to make good progress in the current AM industry. As a result, it is important to collect relevant important information in an article/book chapter, so that future researchers find it useful. Therefore, the objective of this book chapter is to include the state-of-the-art review on the areas of additive manufacturing of polymer composites.

2 Current AM Technologies for Composites

There are different types of additive manufacturing technologies which have been used to composite printing. Based on available technologies, it can be divided into four major categories. Solid based, liquid based, powder based, and hybrid based additive manufacturing [4]. Figure 2 shows the young modulus of thermoplastic polymers with a comparison with other widely used metals in different high-performance applications like aerospace, automobiles, sports, medical instruments etc. In the following sections, an overview of different AM processes for 3D printing of polymer composites has been included, and they are discussed according to four categories: solid based, liquid based, powder based, and hybrid based additive manufacturing.

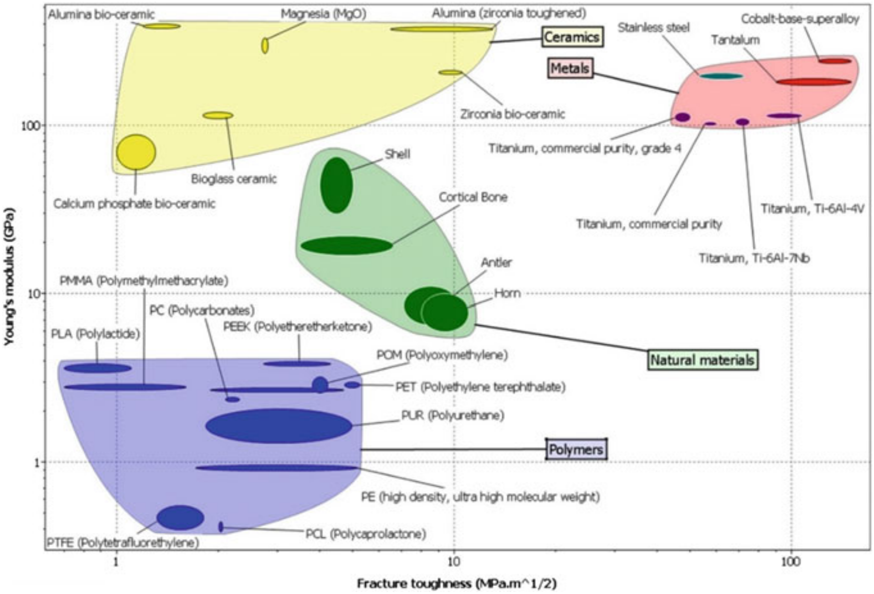


Fig. 2 Mechanical properties of potential materials in comparison with bulk materials for composite-based additive manufacturing [5]

2.1 *Solid Based AM of Composites*

2.1.1 Fused Deposition Modelling (FDM)

The most commonly used solid based AM process is the fused deposition modelling (FDM). FDM works with layer-by-layer printing to make three-dimensional (3D) objects with the help of computer aided design (CAD) software. FDM is sometime refer to Fused Filament Fabrication (FFF) where filaments are melted and extruded via a nozzle for layer deposition. Mixture of melted liquified materials are deposited and solidify with the previous layers in the base platform to form the final object. Materials suitable for FDM are mostly thermoplastics, like, acrylonitrile–butadiene styrene (ABS) and polylactic acid (PLA) along with powder/fiber polymer composites [6], which possess suitable melting and glass transition temperature and flowability in melted or liquified condition. There are different techniques and types of reinforcement materials, such as, particles, long fiber, short fiber etc. Some applications use multi-nozzles 3D printing as well for providing reinforcement in the polymer composites, which enables varying different combination of materials for FDM type additive manufacturing. In spite of the advantage of FDM for its flexibility, it has major disadvantages, such as, poor surface finish, dimensional inaccuracies, heterogeneity and interlayer weak bonding [7]. However, the process parameters of the FDM process have a significant role on the final product's properties, including strength, surface finish, and internal porosity.

Figure 3 shows the basic working principle of FDM type additive manufacturing. There are two different materials that have been used for this fabrication process. One is built material which is used for expected 3D printing shape (as shown in blue). Another one is supporting material which is used as a base or the foundation for the complex shape printing (as shown in yellow). Both materials come as spools, containing filaments of popular sizes 1.75 mm to 3 mm diameter. Liquefier head is used for melting of the filaments which is directed through the nozzle attached to the bottom of the liquifies head. The nozzle has a degree of freedom in X and Y axis and the build platform has a degree of freedom in Z axis which enable the whole setup for desired share of 3D printing with the help of Computer Aided Design (CAD) [9]. Non-machining type post processing techniques, such as, chemical or vapor bath post-processing, can improve the surface roughness of FDM printed polymer composite and minimize the staircase effect, thus improving the overall surface finish ad dimensional accuracy.

During 3D printing of polymer composite with FDM technique, higher nozzle size and increase in layer thickness led to distortion and internal residual stresses. The Taguchi approach and the ANOVA technique were used to investigate the effects of several key elements on surface roughness and dimensional accuracy. The research found that the surface quality could be enhanced by 66% despite possible variations in accuracy due to varied deposition directions [10].

Another version of FDM based AM process is Droplet Based Additive Manufacturing (DBAM), where matrix and filler are placed dropwise instead of the continuous extrusion process. In a recent research work of Guessasma et al., 2022 [11],

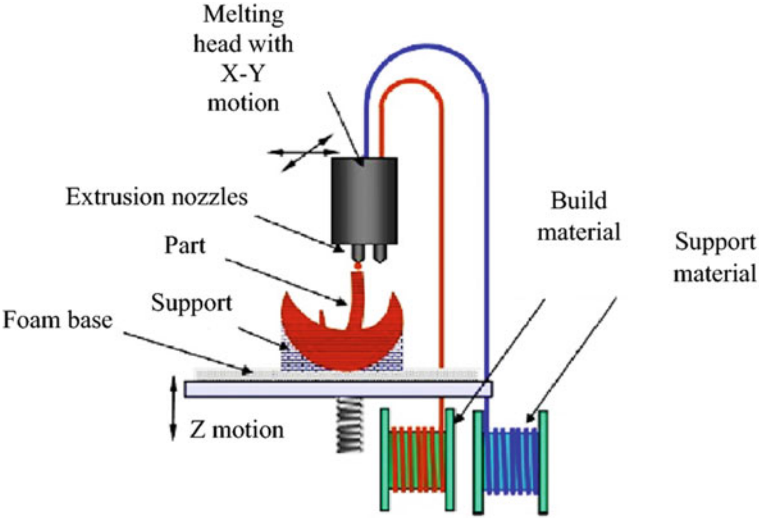


Fig. 3 Principle of FDM [8] (***Open Access***)

the DBAM process was used to manufacture Thermoplastic Polyurethane Elastomer (TPU)/Acrylonitrile Butadiene Styrene (ABS) composite. One of the advantages of using DBAM is to reduce the porosity of the 3D printed composite to 5% or lower. The interfacial behavior of TPU and ABS creates a hindrance of good mechanical performance due to the interface bond. In the study of Guessasma et al., TPU and ABS have not created a strong bond. Creating intertwining droplets leads to creating progressive interface, which may lead to a strong bond. The mechanism of strengthening the bonding between TPU and BAS remains to be a goal of future research [11].

2.1.2 Laminated Object Manufacturing (LOM)

Laminated object manufacturing (LOM) uses a sheet lamination process to create solid, three-dimensional objects where adhesive-coated thin film material has been used. Layers of the adhesive-coated films adhere to one another, and the film is then sliced to the desired pattern using a laser beam. This method is extremely adaptable and can involve a wide range of materials, notably the long fibers that are used as reinforcement in composites [12].

Figure 4 illustrates a common LOM process where a heated roller is used to laminate a sheet to the previously laid layer where the bonding will take place. The layer sheet has a thin coating of thermoplastic adhesive on the down-facing surface, and the roller rolls over it with applying heat and pressure. After the application of the roller, a focused beam of laser cuts the last implemented layer into desired dimension and then waste take up rolls collect the wastage part and help to place the new sheet from the material supply roll by pulling the sheet. This process is repeated until the desired dimension is achieved.

2.2 *Liquid Based AM of Composites*

2.2.1 Stereolithography (SLA)

Stereolithography (SLA) is becoming popular for its fabricated part quality and surface finish compared to widely used FDM process. In this method, successive layers are placed one after another and selective curing is carried out in liquid photopolymerizing resin with controlled UV laser beam [14]. Figure 5 represents a schematic set up of SLA process, where a low power UV laser beam helps solidify a thin layer on the build platform. The widely used liquid photopolymerizing resins are acrylic and epoxy resins [15]. X–Y scanning mirror is moving in X and Y direction to deposit the layer of desired dimension. Build platform moving in Z direction to submerge the 3D printing object inside the resin. For every layer deposition, build platform go down and rollers moved over the next layers.

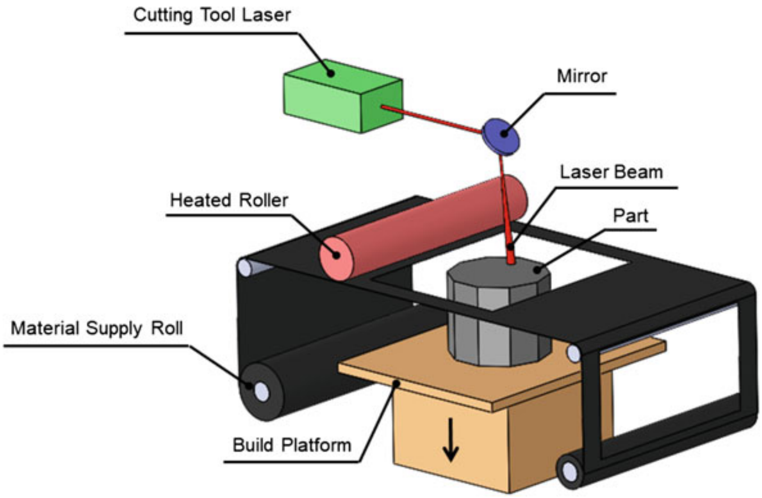


Fig. 4 Laminated object manufacturing (LOM) [13] (***open access***)

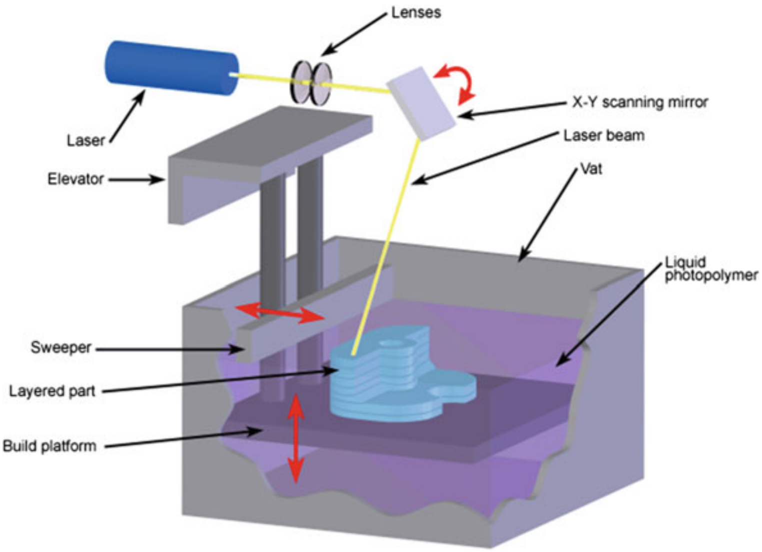


Fig. 5 Schematic of SLA [16] (***Open Access***)

Wang et al. [17] has done some research on how to improve dielectric properties of additively manufactured composite using SLA method of 3D printing. To make methacrylate malate photocurable resins (MMPR) UV curable, synthesis with malic acid has been tested. Bio-fillers cellulose nanocrystals (CNCs) powder's reactivity and solubility has been improved with the use of methacrylic acid (MAA). It was observed that CNCs-MAA had played an important role in increasing the polarity inside the composite by a small group which resulted in an increase in the dielectric constant. Thus, enhancement of capacitance by 132% compared to the mother composite polymer has been observed [17].

2.3 Powder Based AM of Composites

2.3.1 Selective Laser Sintering (SLS)

Selective Laser Sintering (SLS) is powder bed fusion-based 3D printing process where laser beam is used to bind the photopolymer powder to form polymer composite by fusion. The temperature generated by laser source is slightly below the melting temperature of the polymer and reinforcement fillers for uniform distribution of heat during sintering. Figure 5 shows the basic principle of SLS process where the work bench is submerged into powder. One of the major benefits of SLS is that it does not need any supporting structure like the FDM process [18]. Figure 6 illustrates the 3D printing setup by SLS technique. Two types of platforms are used to maintain a level of powder. The fabrication platform can move in Z direction for lowering down after formation of one layer by fusion by the laser source and give the space for the powder to form the next layer. The roller rolls in X direction to distribute the powder evenly. The scanner system can move in X and Y direction to direct the laser power for layer deposition.

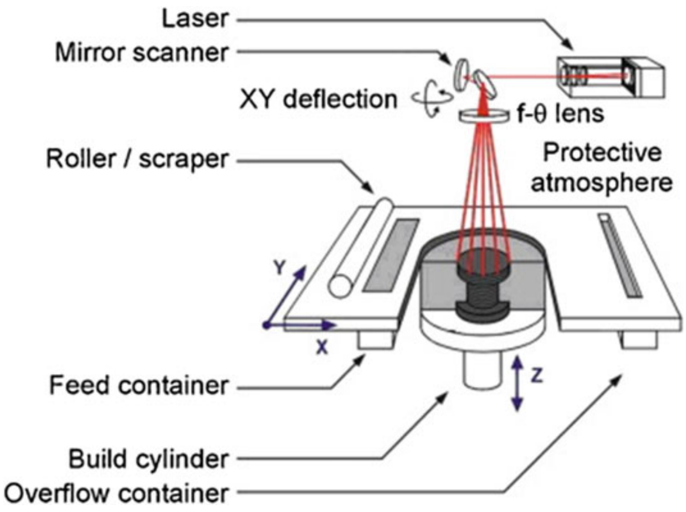


Fig. 6 Schematic diagram of SLS 3D printing process [19]

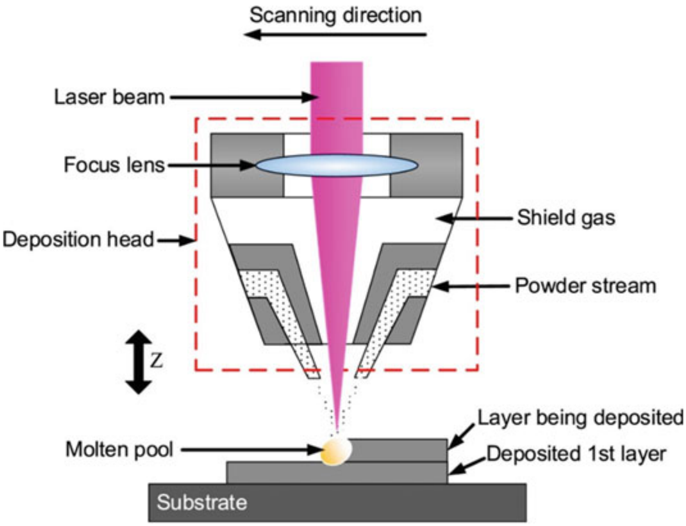


Fig. 7 Schematic diagram of LENS 3D printing process [20]

2.3.2 Laser Engineered Net Shaping (LENS)

Laser engineered net shaping (LENS) is the AM technique which is usually used to make 3D objects with metal alloys and metal composites via melting of metal powders (mostly Titanium, Nickel, Zirconium etc.) with laser beam. However, this has the potential to be used for the 3D printing of polymer composites. Figure 7 indicates the schematic arrangement of LENS AM where metal, or polymer powders are directed through the powder stream and melted by the heat of focused laser beam. The deposition head has the XYZ degree of freedom to move along the trajectory to print the 3D object. Shield gas (usually Argon) is used to ensure minimum oxygen presence to prevent oxidation of molten pool and it becomes solid when laser beam moves away, and it can dissipate the heat. Repetition of this process finally produces the desired object as instructed by CAD.

2.4 Hybrid of Powder-Liquid AM in Composites

2.4.1 Three-Dimensional Printing (3DP)

Three-dimensional printing (3DP) is a similar technique as SLS, where liquid binder replaces the laser system using the inkjet printing technology. In order to create a solid pattern for one layer, the liquid binder is selectively poured on a powder bed in printing trajectory. 3DP can use a wide variety of materials including from metal, polymer, ceramic, and composites based on the binding ability of liquid binder-powder reaction to form a solid layer. Surface finishing mostly depends on the particle size (<20 μm) for this printing technique. 3DP manufactured object has a common tendency of being porous compared to other AM techniques, which is why post-processing by sintering has been used to reduce the porosity of materials. However, post-sintering led to distortion in the object which make 3DP difficult to maintain geometrical tolerances [10]. In order to avoid this, infiltration technique can be used to fill up the blank spaces in previously 3DP manufactured object by another fillers material or reinforcement, which results in improvement of mechanical properties [21].

3 Reinforcement of Composites in AM

With the relentless efforts of researchers over the past two decades, the additive manufacturing of polymer composites has evolved dramatically. According to end-user needs, a variety of approaches have been used to improve mechanical, thermal, and electrical properties of polymer composites. Figure 6 represents the mechanical properties of widely used pure polymers in 3D printing [2]. It can be said from this plot that PLA is the material of choice over other thermoplastics for not only its biodegradability, but also its superior qualities in terms tensile strength, modulus of elasticity, and flexural strength. In order to enhance the properties of these thermoplastics, reinforcement of comparatively stronger materials is used to make this a composite with superior qualities than the polymer matrix. For the 3D printing of polymer composites, reinforcement typically comes in the form of fibers, particles, or both. Various categories of reinforcement along with methods for enhancing them are covered in the next section.

Figure 8 shows four major mechanical properties: flexural strength, impact strength, modulus of elasticity, and tensile strength of pure thermoplastics matrix materials. In the upcoming section, the methods of enhancing these mechanical properties of polymers further by different reinforcement techniques will be discussed.

3.1 Particle Reinforced Composites in AM

The type of matrix material and the requirement from the end-users influence the selection of reinforcement particles used in polymer composite. Many researchers have employed a few materials, including iron, aluminum, tungsten, ceramics, and glass as particle reinforcement, to enhance the strength and mechanical properties of the polymer composite parts made by additive manufacturing. In recent years, many researchers have been focusing on using various particles to enhance the composites' overall properties. For example, nylon-based composites are found to

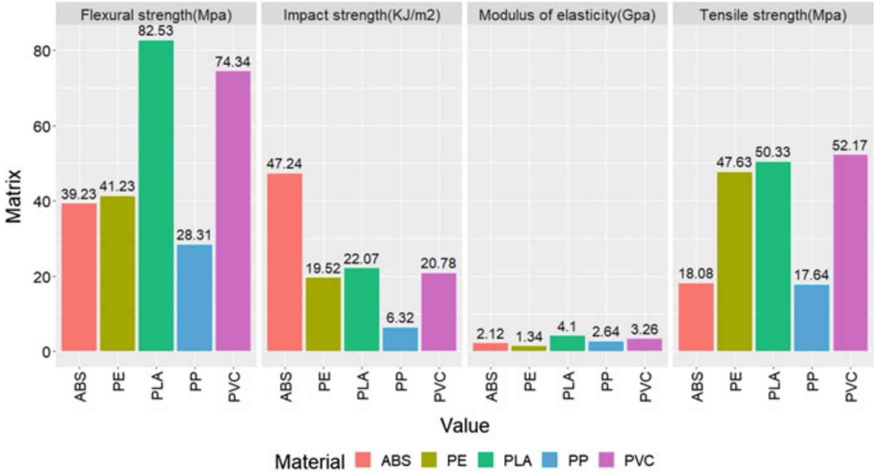


Fig. 8 Mechanical properties of widely used thermoplastic in 3D printing

become stronger when reinforcement particles are added. Both the tensile strength and stiffness of a polymer composite can be improved by adding glass beads as reinforcement in the Nylon-11 matrix, as opposed to an FDM product that is only matrix-based [22]. Nylon-6 combined with aluminum and aluminum oxide particles has the potential to improve the wear resistance and COF (Coefficient of Friction) of nylon-based polymer composite in SLS type AM [23].

Additively manufactured (AM) PLA Composite by FDM has been studied with different particles reinforcement. With the increase of magnesium (Mg) particles from 2 to 6 wt%, both ultimate tensile strength (33.5 to 38 Mpa) and tensile modulus increased (0.85 to 1 Gpa) compared to those properties of pure PLA. However, further increase in the reinforcement concentration to 8 wt% significantly drops the tensile modulus, even with the increase in ultimate tensile strength [24]. In another study, bronze, copper, magnetic iron and stainless-steel particles have been used with PLA matrix to improve the print height and overall mechanical properties of the AM PLA composite. It is observed that inclusion of metal particles has increased the overall mechanical properties. Brass reinforced PLA (Br-PLA) has achieved higher young's modulus of 5401 MPa compared to other composites (Cu-PLA, MI-PLA, SS-PLA) in this study. On the other hand, magnetic iron reinforced PLA (MI-PLA) shows promising results in terms of ultimate strength and fracture toughness which is 39 and 3.4 MPa $\sqrt{m}$ respectively [25].

Typically, metals or their oxides are utilized as reinforcement in FDM-type additive manufacturing for ABS composites. In the ABS matrix, $BaTiO_3$ was employed to enhance the dielectric permittivity and adjustable effective permittivity [26]. It is found that particle reinforced ABS can enhance the young modulus and thermal conductivity, when iron and copper particles are used as reinforcements respectively [27, 28]. The thermoplastic elastomer has been employed [29, 30] to reduce anisotropy in various 3D printing orientations. Added titanium oxide to ABS boosted tensile strength, however, made the composite more fragile [31].

3.2 Nanofiller Composites in AM

In the field of AM polymer composites, nanofillers are gradually gaining popularity for the development of nanocomposites. In composites, there are four different forms of nanofiller: organic, inorganic, carbon nanostructure, and clays [23]. Nanofillers can be used to improve composites' mechanical, electrical, chemical, and thermal characteristics without significantly altering their weight [32]. Among others, the most well-known additive manufacturing techniques that use nanofiller as reinforcements include FDM, SLA, and LDM processes.

PLA nanocomposites are becoming an emerging field of study for many researchers. Because of its biodegradability and appropriateness for use in the biomedical and food sectors, PLA stands out from other thermoplastics on the market [33]. Hydroxyapatite (HA) has been found to successfully improve the mechanical strength and biocompatibility of PLA composite. Researchers have tried different HA concentrations to check its influence on the PLA composites. In comparison to the individual strengths of components, composites with a 30% HA content had the highest compression, flexural and impact strengths among all the materials studied (0–30 wt% of HA) [34]. In another study, 3D printing of bone implant has been attempted with HA-PLA composite for different wt% of HA (i.e., 5, 10 and 15%), which shows improvement in the mechanical characteristics of bulk and 3D-printed trabecular bone model, although the printing quality is found to degrade with the increase of HA contents [35]. In recent studies, PLA matrix and carbon nanotube (CNT) reinforcement are used to make CNT-reinforced PLA composite using the SLS AM method. It is reported that CNT aids in improving the mechanical performance, increasing the Young's modulus by around 17% for 0.1 wt% and by an additional 20% for 0.2 wt% compared to the pure PLA [36]. The ultimate tensile strength was boosted by 10% from 86 MPa, while elongation lowered from 11 to 9%, when CNT concentration was raised to 0.5 wt%. Inclusion of Nano-clay (Cloisite 30B) in PLA composites resulted in improvement in dynamic mechanical properties, such as, 15% increase in modulus of elasticity with better shape stability during printing [37]. The PLA–CNT composites in the FDM process at a CNT concentration of 1 wt% showed relatively better mechanical properties for the range of CNT concentration tested (0.1 to 1 wt%). The infill of a honeycomb structure during the printing of PLA composites has also demonstrated encouraging mechanical and thermal stability features. [38].

Addition of $ZnFe_2O_4$ particles (0–14%) in AM ABS composite helps to increase overall mechanical and thermal properties, such as, 52% increase in tensile strength, 87% increase in thermal conductivity, and 75% increase in hardness [37]. With multi-wall carbon nanotube (MWCNT) coating during FDM, ABS composite also showed a substantial increase in tensile strength. Printing with FDM using 15wt% MWCNT with 5% proprietary adhesive and 80% ABS resin demonstrated a 25.6%

raise in tensile strength and a 5.65% increase in elongation [30]. Even the 1% Nano MMT (montmorillonite) reinforcement with ABS demonstrated a 25.8% higher tensile strength and a 17.1% increase in flexural strength, outperforming the other combination of this study with the 1% MWCNT, SiO_2, and $CaCO_3$ reinforcements.

Since graphene particles block the UV signal, utilizing SLA to polymerize composites with more than 5 weight percent of this nanofiller can be difficult [26]. The use of graphene oxide (GO) with only 0.2% can improve the mechanical characteristics, such as tensile strength by 62%. In addition, the use of GO as reinforcement improved plasticity in order to get over the restriction of strengthening by graphene particles [39]. Another study for PLA composite via FDM process found that 0.2 wt% graphene content yielded superior results than 0.1 and 0.5 wt% of graphene content. The 0.2 wt% graphene content resulted in an increase in elastic modulus by 17% and an increase in ultimate tensile strength (UTS) by 47%. Reduced graphene oxide (rGO) particles have also been used as reinforcements with PLA and ABS composites to improve the electrical properties of the AM composites [40].

In SLS AM, nanosilica, MWT (Montmorillonite), CNF, MWCNT particles have been used with PA composites. For nanosilica-PA12 (Nylon-12) composite, it was found that there are increase in tensile strength, tensile modulus, and impact strength by approximately 20%, 40% and 9.5%, respectively [41]. However, adding Multi-Walled Carbon Nanotubes (MWCNT) at a concentration of 0.1 weight percent to PLA composites increased the materials' Young's modulus and UTS by 26% and 41%, respectively [30]. However, the elongation of PLA composite with graphene and MWCNT decreased. The polyvinylidene fluoride (PVDF) with zirconium tungstate particles were found to have good printability and dimensional stability, while lowering the mechanical properties [42].

3.3 Fiber Reinforced Composites in AM

In both conventional manufacturing and additive manufacturing, fibers serve as a common reinforcing element for composites. When compared to conventional molding composites, the main drawback of AM objects is the interfacial connection between the 3D printed path and interlayer, and porosity [43]. During the 3D printing process, FDM has the capacity to handle both short and long fibers. Fibers can be added to the polymer matrix to enhance their mechanical, electrical, thermal, and geometrical accuracy [10]. Continuous fibers can withstand higher tension loads when load is applied to the composite in parallel to the fibers. As it produces better mechanical performance in tensile loading than the other configuration of composites, continuous fibers have gained popularity among many researchers for their outstanding enhancement in mechanical properties.

Figure 9 represents the preparation of feed stock by extrusion for any thermoplastics used in additive manufacturing. There is a hopper to feed the expected materials to feed in the form of resin or powder. Heaters are used to soften these materials and screw act as a pusher to compress and pass through the nozzle of user specific size.

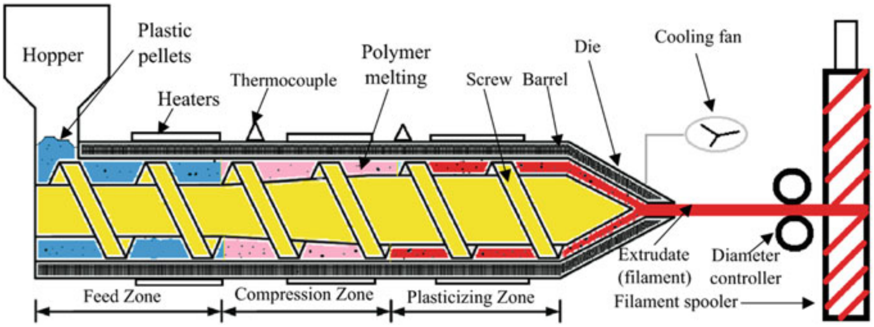


Fig. 9 Schematic diagram of extrusion process for making matrix and reinforcement spool for 3D printing [44]

Finally, a diameter controller will be in action to control the feed stock diameter with tolerances. Discontinuous or particle-based reinforcement (i.e., short carbon fiber) can be used to create the feed stock or filaments which will be used for 3D printing.

Different techniques have been adopted in FDM to add short fiber, long fiber and continuous fiber in polymer-based composite. Figure 10a represents the short fiber reinforced polymer (SFRP) printing where a single nozzle has been used to print. In feed stock short fiber has already been placed inside the roll during extrusion process. Figure 10b, c represent the continuous fiber placement via one nozzle and two nozzles respectively in FDM type AM. For single nozzle, continuous reinforcement has been placed together with the melted matrix. Fiber is placed in the printed object in the same raster angle as the nozzle path. Whereas with two nozzle systems, matrix and continuous fiber can be placed independently in different locations of the layer, which adds additional flexibility in designing AM composite parts.

3.4 Inorganic Fibers Reinforced AM Composites

Fibers used for AM polymer composite can be broadly divided into two types: continuous and discontinuous fibers. A continuous fiber reinforced polymer composite prototype was created and patented in 2014 using traditional tape placement and the FDM printing technology via material extrusion. During this 3D printing method, the matrix is melted and continuously supplied by one nozzle while continuous fibers are fed by another. Carbon fiber, glass, kevlar, jute, ultra-high molecular weight polyethylene (UHMWPE), and other continuous fibers are commonly utilized in 3D printing processes. The tensile strength of carbon, glass, UHMWPE and kevlar fibers ranges from 2.20 to 3.5 GPa. Alternatively, jute fiber from natural resources has a lower tensile strength of approximately 0.42 GPa than other fibers. Carbon fiber is the most popular reinforcement material for 3D printed composites because of its stiffness and strength [46].

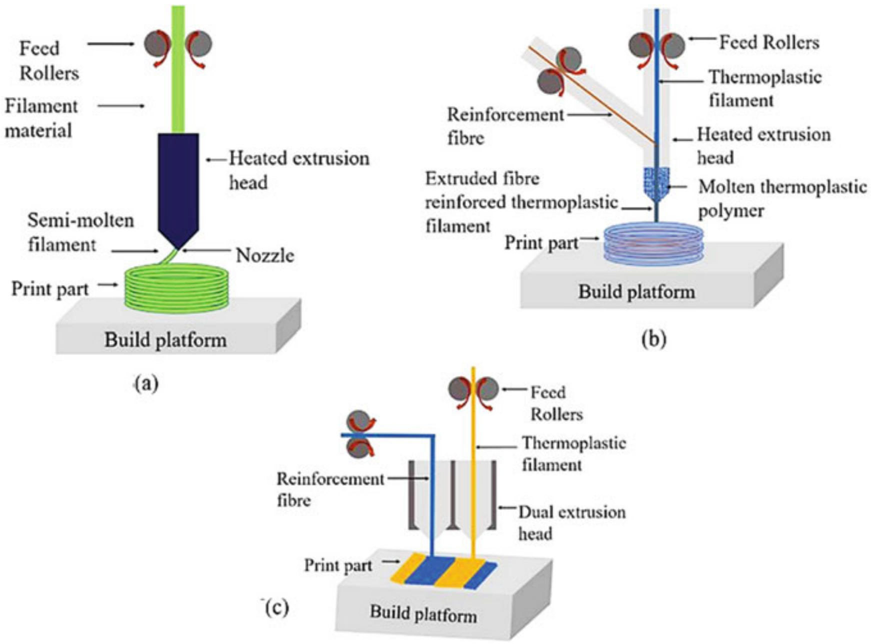


Fig. 10 **a** FDM printer for polymers and SFRP. **b** Co-extrusion FDM printer for CFRP. **c** Double nozzle-extrusion FDM printer for CFRPs [45] (***Open Source***)

There are mainly two types of inorganic fibers: continuous and discontinuous fibers. Figure 11 presents the mechanical properties of polymer composites with inorganic fibers in FFF type AM. It can be seen from the plot that researchers have tried different combinations of fibers in mostly three thermoplastics (ABS, PLA and Nylon). Carbon fiber with epoxy resin base has constitute stronger composite than other studied thermoplastics. Nylon composites also have good mechanical properties with fiber reinforcements [47].

There are different 3D printers available on the market which are composite specific. There is no single printer that can handle all types of composites. Figure 12 illustrates these printers' capability of printing different composites. Among them, Markforged has the versatile capability of printing nylon composites with glass fiber (GF), carbon fiber (CF) and kevlar reinforcements. 3DXTECH can handle carbon fiber and glass fiber with different thermoplastics to manufacture polymer composites.

Peng et al. performed research on the short carbon fiber reinforced composite with nylon matrix in FDM AM in 2022 [48]. This study aims to investigate the behavior of printed gyroid structures under compression and buckling stresses. Figure 13 shows SEM images of FDM fabricated gyroid structure which seems to be a complex geometry for FDM printing. The investigation showed that the direction of the printing

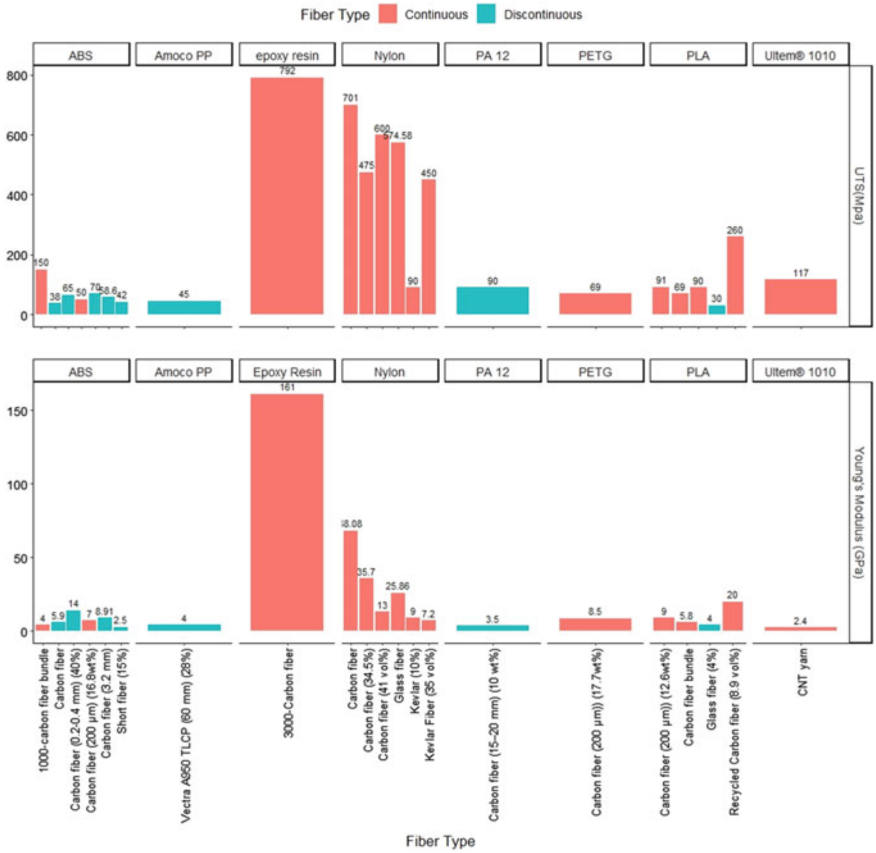


Fig. 11 Mechanical properties for different type of inorganic fiber with commonly used thermoplastic for FFF based additive manufacturing

process affects Young's modulus of this construction. Printing's compressive properties are influenced by the number of unit cells applied [48]. In 2022, Li et al. [49] reported 3D printing of continuous carbon fiber (CCF) reinforced onyx (CCF/Onyx) thermo-plastic composite fastener (TPCF). The 'Onyx' filament was a mixture of chopped carbon fiber and nylon matrix. In addition to using 'Onyx', continuous carbon fiber was used for reinforcements in critical locations. Investigations have been conducted into the part's durability and the reason for failure when used in a single lap joint. The stiffness and strength of fasteners increased by 73% and 196%, respectively, as compared to a short carbon fiber-based composite, with the volume addition of 40% CCF. With the use of heat treatment, the prior increment was increased by an additional 20.35% [49].

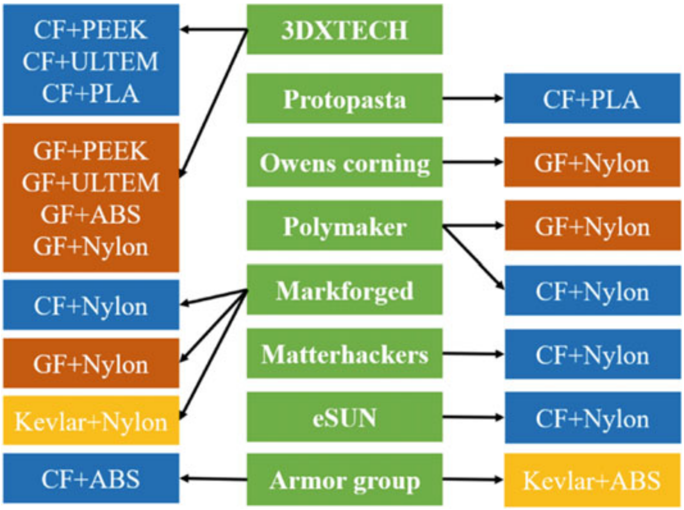


Fig. 12 FDM with composite with 3D printing machine; fiber: Carbon fibre (CF), Glass fibre (GF) and Kevlar (KF); matrix: polyether ether ketone (PEEK), acrylonitrile butadiene styrene (ABS), polylactic acid (PLA) and nylon [45] (***Open Source***)

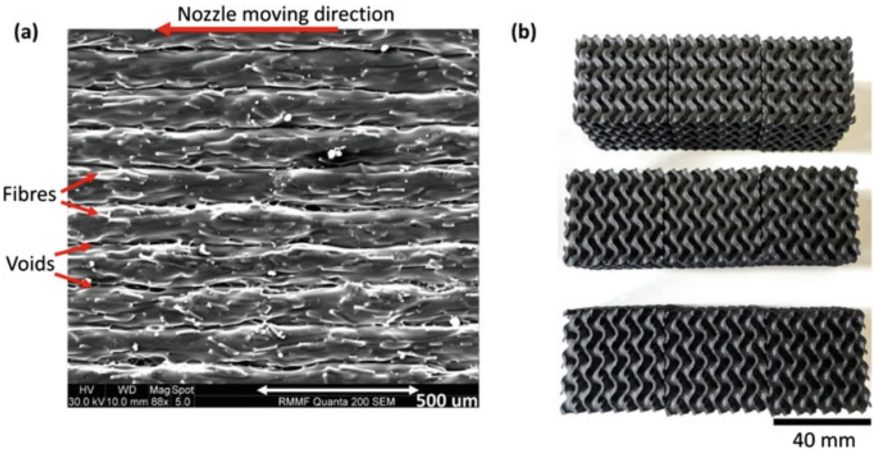


Fig. 13 SEM image of composite by FDM; (b) fabricated gyroid structures samples [48]

3.5 Natural Fibers Reinforced AM Composites

Natural fiber has become popular in the field of 3D printing of bio-composites. The process of manufacturing natural fiber reinforced polymer composites can be considered as a sustainable manufacturing process. Natural fibers are gathered from nature, more especially, from the environment, animals, and plants. Natural fibers are more desirable than inorganic fibers due to their biodegradability and recycling potential [50]. The output of natural fibers exceeded 113.6 Mtons (million metric tons) in 2021 [51], which makes it clear why there is an increase in the usage of natural fiber globally. For the majority of natural fiber reinforced composites, the zone around the interface is the primary area of concern due to stress concentrations triggered by weak interfaces, leading to poor mechanical characteristics. Weak interfaces are frequently internal defects caused by insufficient adhesion between the fibers and the polymer matrix or porosity brought on by gas diffusion [52]. The interfacial cohesion may be improved not only through modifying the surface properties but also by choosing the appropriate filler and matrix combinations, and the fiber content acts an essential part in enhancing mechanical performance.

The starch composite gel has been evaluated for additive manufacturing by Cui et al. [53], and it has a promising printability. In order to examine the behaviors of the resulting gel in terms of hardness, gumminess, apparent viscosity, and springiness, the levels of sodium alginate and xanthan gum have been varied in a starch composite gel made of potato starch, sodium alginate, xanthan gum, and water in a specific ratio. By adding the right amount of thickening agent to the mixing solution before 3D printing, morphological stability has been improved after printing [53].

Figure 14 shows the combination of commonly used thermoplastic and its natural fiber-based composites [2]. The PLA–Bagasse has the highest flexural strength of value 91.25 MPa and modulus of elasticity 8.2 GPa, whereas PE–Kenaf composite has promising tensile strength and impact strength 93.4 MPa and 87.1 kJ/m^2 respectively.

4 Effect of 3D Printing Parameters on AM Composites

During additive manufacturing of polymer composite, 3D printing parameters play a vital role in the quality of the printed composite part. First, the composite part was designed by computer aided design which was later converted into STL file. This STL file is later fed into the printer specific slicing software to create the G-code (geometric code) for the 3D printer. 3D printer will follow the G-code and will fabricate the parts by following raster pattern by the nozzle. Figure 15 shows different printing parameters which can be broadly divided into two categories. These are device parameters and laying parameters. Nozzle related parameters like nozzle size and nozzle temperature belong to device parameters. In addition to this, platform temperature is one of the key device parameters which has an influence on the 3D printed parts. Laying parameters consists of infill pattern and density with air gap, raster angle and orientation with perimeters, layer height and width etc. Figure 15 represents the schematic diagram indicating all layering parameters that are used to move the build platform in X, Y and Z direction. The common parameters that influence the part quality are infill pattern, infill density, void content, and raster angle.

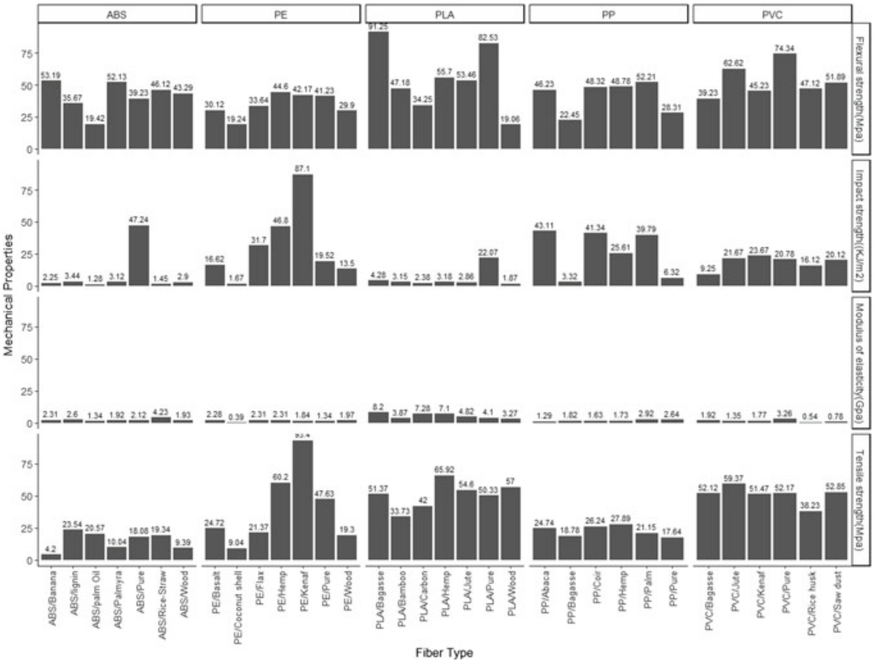


Fig. 14 Natural fiber source and its composites

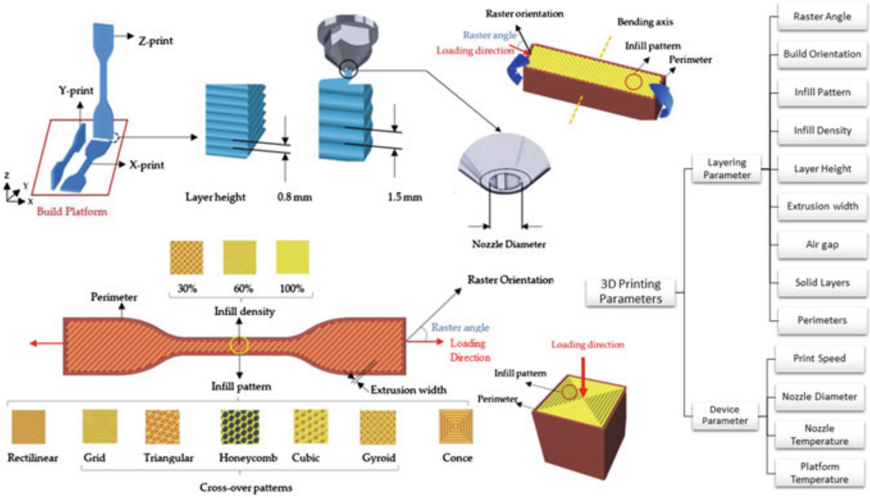


Fig. 15 3D Printing parameters during additively manufacturing [54] (***Open Access***)

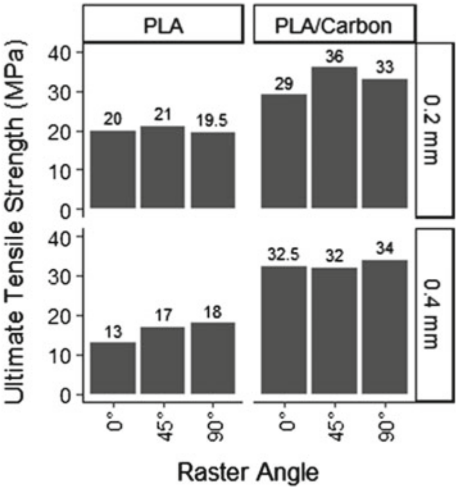


Fig. 16 Ultimate tensile strength of PLA and PLA/short carbon composite based on different raster angle and printing layer height

To understand the effect of printing parameters on the properties of AM parts, Kovan et al. [55], had carried out 3D printing of Neat PLA and PLA/short carbon fiber reinforced composites with three widely used raster angles and with two-layer thicknesses of 0.2 mm and 0.4 mm. He studied the ultimate tensile strength (UTS) for these cases. Figure 16 shows the comparative UTS for different combinations of raster angle and layer thickness. It was found from this study that for lower layer thickness for both PLA and PLA/Carbon composite, higher UTS found at raster angle of 45 degree and with the reinforcement with short carbon fiber. The combination of lower thickness with 45-degree raster angle results in approximately 71.5% increase in UTS for the short fiber reinforced PLA/carbon composite, which is the highest among all cases tested. However, for layer thickness of 0.40 mm, raster angle of 90 degree resulted in higher UTS than others for both pure PLA and PLA/Carbon composites. Separation between layers is prominent due to the presence of short carbon fiber in the PLA/carbon composite.

Peng et al. [56], 2021 has studied the effect of printing parameters on mechanical properties of PEEK and its composite with carbon fiber and glass fiber. It can be observed from Fig. 17 that UTS, flexural strength and impact energy decrease with the increase of layer thickness and printing speed, whereas increase with nozzle temperature and platform temperature. The optimum point of mechanical characteristics of printed CF/PEEK and GF/PEEK are found at a platform temperature of 280 °C and a nozzle temperature of 440 °C. This is because higher nozzle temperature enhances the fluidity and formability through melting for printable feedstock. A hotter platform ensures infiltration and diffusion between deposited filaments and interlayers by providing additional heat energy to it. As a result, this combination helps to increase interlayer adhesion and decrease internal porosity. On the other hand, higher printing speed and layer thickness have detrimental effects on the printed parts. Slower printing speed and smaller layer thickness lead to stable printing path

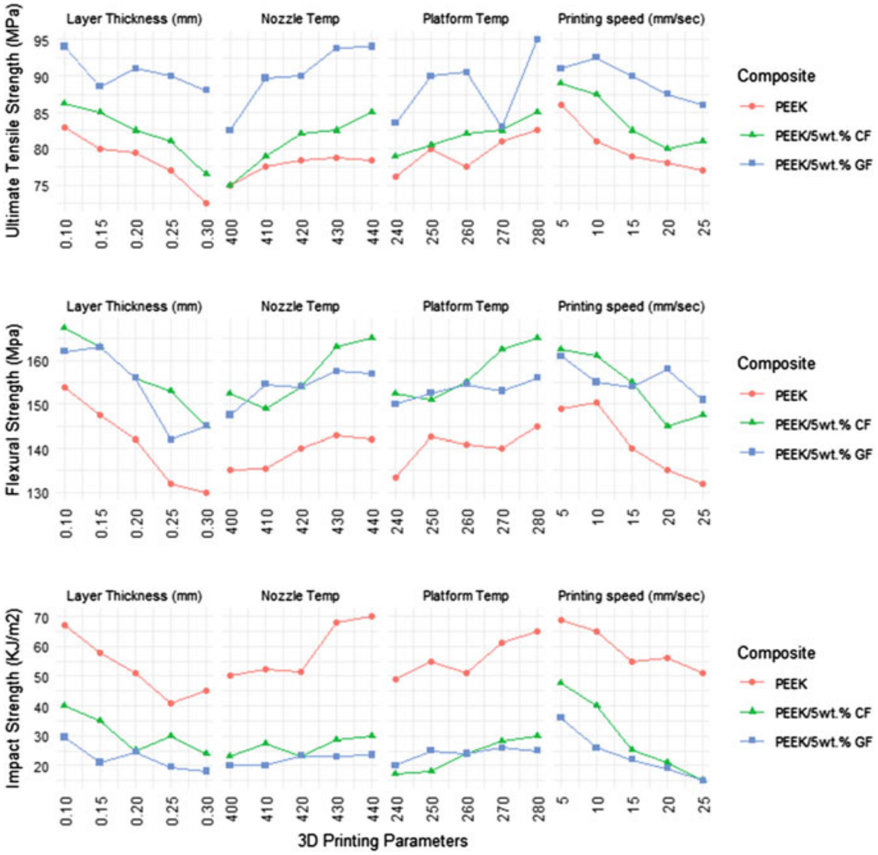


Fig. 17 Mechanical properties of PEEK, PEEK/CF and PEEK GF composite based on different printing parameters

with better extrusion capability and increase the adhesion characteristics with other layers.

5 Post Processing of Composites in AM

To implement faster manufacturing of user specific complex geometry, additive manufacturing is becoming popular over the traditional manufacturing process. Fused deposition modeling (FDM) is the most widely used 3D printed technique adopted by many users of different fields. One of the major concerns related to 3D printed objects is the surface finish of the printed part, which is mostly due to the staircase effects. In order to reduce these staircase effects, various strategies can be implemented. However, some of these strategies may start affecting the geometrical tolerances and others may change the mechanical properties of the object by adding more heterogeneity in the composition of the additively manufactured polymer composites. Dimensional accuracy or tolerance of the printed polymer composite parts remains to be another challenge or shortcoming for 3D printing of fiber reinforced polymer composites.

Surface roughness produced by additive manufacturing processes affects the end product's appearance and functional use. The surface quality can be improved using post-processing methods including sand blasting, polishing, machining, or chemical treatments. In addition to this, post processing like annealing or heat treatment enhances the mechanical properties by improving toughness, stiffness, and strength of printed parts. Furthermore, dimensional accuracy is one of the major problems for 3D printed parts. Surface grinding, trimming or subtractive machining need to be used to achieve the geometrical tolerances as per user specification. The moisture absorption of polymer composites leads to altering the dimensions which degrades the overall load bearing capabilities. In order to protect from this problem, watertight coating or sealing is usually used in 3D printed parts. In the following section, a brief overview of different post-processing techniques is provided.

5.1 Chemical Post Processing

Acetone is a widely used chemical for the chemical treatment of 3D printed polymer composites which improves isotropy of the composite by improving the surface finish significantly (97%), although the better mechanical properties become weaker for the chemical reaction [57]. In this process, the 3D printed object either is submerged into a chemical solution for a definite time or chemical can be supplied in the form of cold or hot vapor. Sometimes chemicals are used to increase the fiber-matrix bonding, resulting in reduction in fiber pull out defects in the 3D printed fiber reinforced polymer composites [45].

5.2 Laser Treatment Process

Additively manufactured polymer composited often treated for surface roughness by laser exposure with a specific curing time. As shown in Fig. 18, by laser power, heat is generated and staircase like roughness melts and forms a relatively plain surface, which results in a better surface finish for this object [58]. From the study of Chen et al. (2019), Laser treatment in Aluminium fiber in PLA Matrix had not only improved the surface finish but also improved the tensile strength of PLA/Al composite.

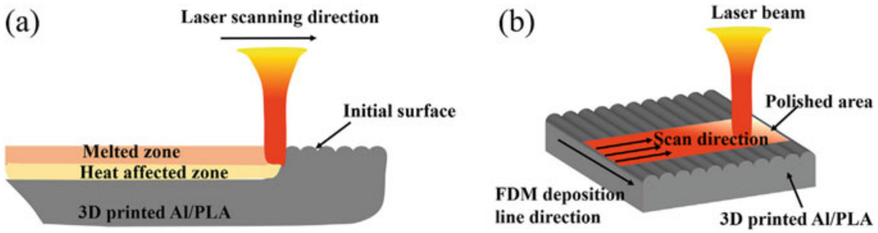


Fig. 18 Schematic representation of the remelting mechanism (**a**) and scanning direction and FDM deposition line direction (**b**) [60]

A recently adopted technique by AREVO company showed reduction of porosity the polymer composite parts in Directed Energy Deposition (DED) method. The method aims to reduce the porosity and enable the carbon fiber composite to have nearly 50% fiber in the composite with laser heating and compaction. The end goal is an increased specific strength of the AM composite object [59].

5.3 Heat Treatment Process: Annealing

Heat Treatment is one of the most popular post processing methods to improve the overall performance of an AM composite, especially those fabricated by the FDM technique. Heating above the glass transition temperature makes it possible to fill up the void and recrystallization helps to create better surface finish with improved mechanical characteristics. As shown in Fig. 19, post processing by heat treatment and chemical treatment impacted the surface finish and void formation. A temperature window can be selected for a specific composite for postprocessing heat treatment. For example, a temperature between the glass transition temperature of matrix polymer and material softening temperature where the 3D printed object starts deforming can be used for heat treatment. The suitable annealing temperature can shift in between the glass transition temperature and cold crystallization temperature for semicrystalline polymer composites [61].

5.4 Ultrasound Treatment Process

Ultrasonic vibration during the FDM AM process helps to create compact layers with reduced porosity without altering other characteristics of AM objects negatively. Maidin et al. (2015) had found in their study that 21 kHz ultrasound vibration provided better surface finish for PLA composite [62]. Figure 20 represents an actual set up where ultrasonic vibration has been applied on the paste color joints for void reduction.

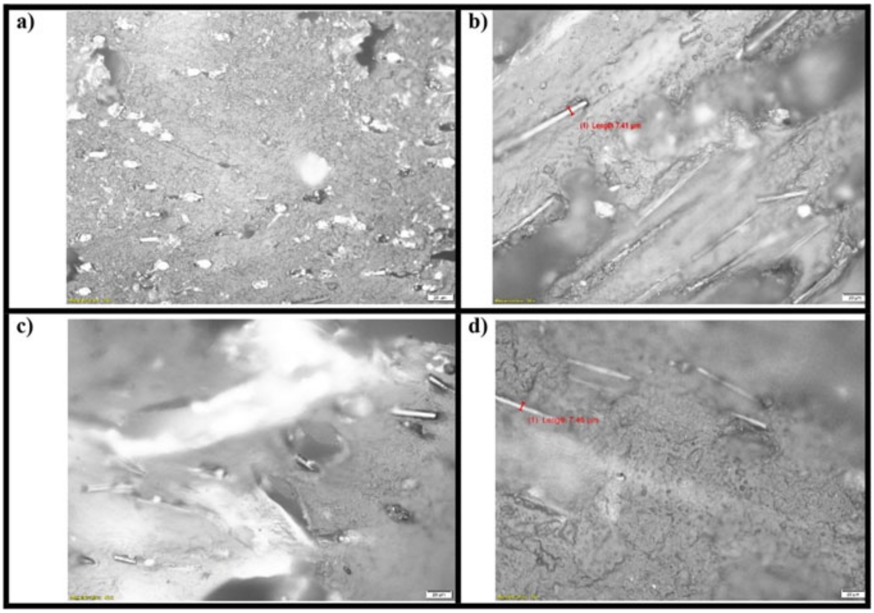
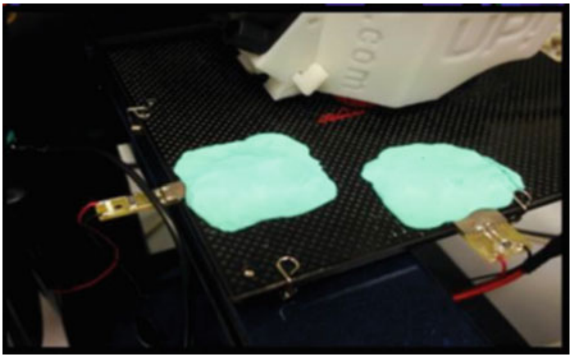


Fig. 19 SEM images for tensile specimen PLA matrix (20 µm) and carbon fiber (10 µm); heat treated: **a** section **b** surface; chemical post processed: **c** section **d** surface [61]

Fig. 20 Representation of ultrasound treatment during FDM 3D printing [45] (***Open Access***)



5.5 Post-processing with Machining

In addition to the existing challenges of dimensional accuracy and surface finish, AM objects may need machining, i.e., drilling, milling, turning, surface grinding, etc., for the sake of fitting in an assembly or to make these objects functionally usable. Machining operations are extensively used in aerospace and automotive industries to machine conventionally manufactured laminated fiber reinforced polymer composites [63]. As a result, there is a potential of using machining as a post-processing technique for 3D printed polymer composites.

Milling operation is mostly used for two purposes in the milling of fiber reinforced polymer composite: one is slot milling to machine slot inside the workpiece and the other is edge milling to finish the outer surface of the part to meet geometrical tolerances. FDM is the most commonly used 3D printing technique for composite additive manufacturing, whereas thermoplastics are the material of choice for composite 3D printing for its low melting point and bonding nature with reinforcement. These characteristics of thermoplastics make these composites suitable for additive manufacturing, however, making this more challenging for traditional machining. Cococcetta et al. [63, 64] studied the slot milling operation of 3D printed carbon fiber reinforced polymer (CFRP) composites for different lubricant conditions: dry, MQL and cryogenic machining. Cryogenic machining showed promising machining outcome in slot milling operation of CFRP with better machined surface and lower tool wear. In order to understand machining behaviors, researchers are working on predictive modelling with the help of the Finite Element Method. Hassan et al., has developed a model to simulate the behaviors of both laminated and 3D printed CFRP composites and was able to find out the physics involved in decohesion and delamination evolution during the micro slot milling operation of 3D printed CFRP composites [65–67].

Rao et al. [68] has studied the effect of conventional drilling process on the 3D printed polymer composite in tension and compared this with AM-fabricated hole during 3D printing. Figure 21 illustrates different types of conventional drill bit tested in their study. The nylon matrix with chopped carbon fiber (ONYX) and continuous glass fiber (CGF) were added to print the polymer composite. After that the printed samples were tested for tensile strength with the variation of 3D printed parameters., i.e., infill density, the pattern of printing, raster angle etc. [66]. It was found that conventionally drilled composite can take higher strength (118 MPa) than the 3D printer fabricated holes (108 MPa). For infill density of 50% and 0-degree raster angle, maximum tensile strength was achieved. Another similar studiy on drilling of 3D printed CFRP composites with different tool geometry has been carried out by the same group of researchers. Slot type drilling showed better performance than the other two drill bits (8 Facet and Dragger type) in terms of geometrical tolerance. However, ‘8 Facet Drill’ showed superior performance on chip removal and contact interaction which showed lower cutting and thrust forces. With the increase of rotational speed, heat generation was high which was due to poor heat removal from the machined surface and chip clogging at higher feed rate.

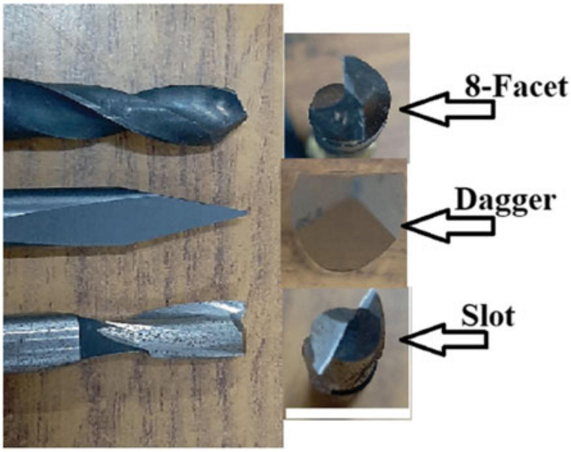


Fig. 21 Different geometry used in CFRP drilling performance [69]

6 Mechanical Properties of Composites

Self-reinforced PLA composite is one of the popular biodegradable composites with the added advantage of recycling [70]. For self-reinforcement of any composite, two versions of matrix materials will be needed. One with relatively high melting temperature as reinforcement and another with low melting temperature which will be used as matrix. In order to use PLA as reinforcement, various treatments are available, such as heat treatment, annealing, etc. Using this reinforcement with semi crystalline PLA and amorphous multifilament PLA, composites with approximately 23% and 41% increase in ultimate tensile strength can be obtained [70].

Another commonly used thermoplastic in Fused Filament Fabrication (FFF) is ABS (acrylonitrile butadiene styrene). The most popular reinforcement in FFF is short carbon (SC) fibers. Many researchers have worked on ABS composites to explore their mechanical properties and other performance parameters and make the carbon fiber reinforced ABS composites useful for industrial application. Iyer et al., 2022 has obtained variation in tensile strength, young's modulus and fracture toughness based on the raster angle of FDM AM of short carbon reinforced ABS (SCRF-ABS). It is intuitive that any composite has the highest strength when load is applied in parallel with the fiber orientation direction or the printing path direction. Elastic modulus, tensile strength, flexural modulus, fracture toughness of SCRF-ABS for raster angle 0° are found to be 4.6 GPa, 31.5 MPa, 47.0 MPa and 3.2 MPa$\sqrt{}$m, respectively. Which are reduced by 35%, 22%, 17% and 19% respectively with the increase of raster angle to 15° [71].

Many researchers focused on using continuous fiber in 3D printing (CF-3DP) to enhance the composites' load bearing properties. Zhuo et al. [72] has studied the use of continuous carbon/ PA6 commingled fibers in 3D printing of polymer composite. Pultrusion is one type of continuous composite manufacturing process with a steady profile of constant cross section, which can be used on mass scale of production. This

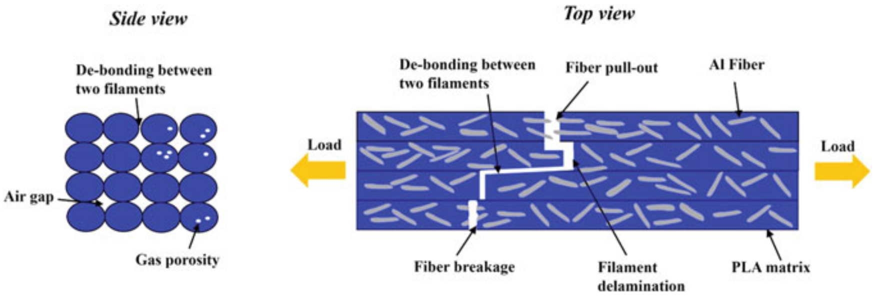


Fig. 22 Illustration of tensile fracture mechanism of additively manufactured Al/PLA composite specimen [60]

method has been used for printing continuous fiber in a commonly used pure plastic FFF printer designed for CF-3DP process. Post processing was followed by heating inside an oven with vacuum bagging to improve the bonding. With a 45% fiber content and 0.5–2% in porosity the printed polymer composite provided a tensile modulus of 61.1 GPa. The tensile strength of carbon/PA6 fiber reinforced composite was found to be 1432 MPa which is 24% lower than PA6 UD tapes composite at 0-degree raster orientation. It has a satisfactory performance of tensile loading toward the reinforcement direction [72].

Figure 22 shows the evolution of different failures in tensile loading of Al/PLA polymer composites. Gas porosities are created due to the temperature gradient after printing, especially when the printed part solidifies. Delamination mainly happened due to the discrepancy between the actual feed rate and predetermined feed rate of feedstock during the extrusion process. Air gaps are mainly generated by the nozzle type and diameter, and printing speed. When these defects persist in AM parts, fracture initiated from one or more defects during tensile testing, which results in fiber breakage, fiber pull out, and delamination [60].

Rimašauskas et al., 2022 has studied 3D printing of PLA composite with continuous carbon fiber in FDM method. Figure 23 represents the flow of experiments, where the main agenda was air void detection by computed tomography and to find its dependence with line width and layer thickness during 3D printing. Mechanical properties are found to be enhanced by using lower line width and layer thickness during FDM process. Among the samples, the best results were reported on 1 mm line width with a thickness of 0.30 mm. For the best 3D printing conditions, tensile strength of 183 MPa and Young's modulus of 23.77 GPa were obtained with the lowest air void volume of 18.5%. A string conclusion from this study is that air void amount can be optimized by changing the process parameters during the 3D printing process [73].

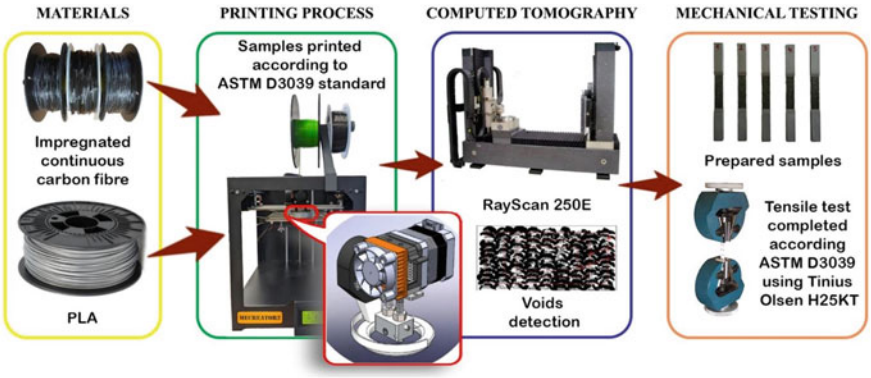


Fig. 23 Research strategy of continuous fiber in 3D printing [73]

7 Latest Research Work on Other Properties Enhancement

Mohan et al. (2022) has reviewed recent research studies and summarized the work on the Aluminium based composite additive manufacturing. They discussed diverse manufacturing techniques to enhance properties of resultant composites in powder-based additive manufacturing (PAM). It has been reported that pre-processing of raw materials, powder morphology and reinforcement types and materials used have a significant impact on composites' microstructure. The surface morphology of the composite depends on the flowability of powders in the 3D Printers. Carbides were frequently used for the PAM process to enhance composite's properties. Titanium and Tantalum carbide are being used to improve the hardness of any composite, whereas Niobium, Tungsten and Silicon Carbide are used for enhancing wear resistance. In order to reduce the oxidation, Hafnium and Chromium carbide are being used as reinforcement for the composites. Zirconium Carbide is used for improving thermal stability, whereas Molybdenum Carbide helps to include exceptional thermal conductivity. In has been shown that 3D printed composites have low power consumption and lesser wastage than conventionally processed metal composites [74].

Almuallim et al. [75] has carried out 3D printing of polymer composites with a goal of enhancing thermal conductivity. In commonly used pristine polymers, the thermal conductivity is in the range of 0.1–0.3 $\mathrm{Wm^{-1}\,K^{-1}}$. In order to increase overall thermal conductivity, aluminum nitride, aluminum oxide, boron nitride, carbon nanotube, diamond, graphene, graphite, metal particles, and silicon nitride are used in the polymer matrix. Commonly used metallic fillers are copper, iron, aluminium, zinc and stainless steel etc. Using copper particles in polypropylene matrix with a filler percentage of 24% resulted in twice the thermal conductivity of the matrix [6, 76]. The filler percentage of 45% resulted in increasing thermal conductivity from 0.24 to 2.45 $\mathrm{Wm^{-1}\,K^{-1}}$ [7, 77]. In addition to this, inclusion of zinc powder with polyethylene achieved 1.7 $\mathrm{Wm^{-1}\,K^{-1}}$ with 20% filler percentage [9, 78]. The most frequently used carbon-based fillers are carbon nanotubes and graphite, based on last two decades' published work. A good thermal conductivity of 695 Wm^{-1} K^{-1} has been achieved with 56% carbon fiber in epoxy resin matrix [10, 79] with low mass density. Graphite filler with polymer matrix resulted in an increase in thermal conductivity from 0.40 Wm^{-1} K^{-1} to 28.3 Wm^{-1} K^{-1} and 0.25 Wm^{-1} K^{-1} to 13.9 Wm^{-1} K^{-1} [12, 80]. In addition to filler inclusion, level of loading, filler type, filler size, and filler shape have a significant impact on thermal conductivity of AM polymer composites.

Nguyena et al. [81], has used FDM process to manufacture GTR-ABS composites by using waste ground tire rubber (GTR) with the ABS matrix. One advantage of this type of filler is that it is inexpensive, increases the reuse potential from automobiles waste, can be recycled, and it decreases the overall weight of GTR-ABS composite. The increased content of GTR content increased the damping capacity of the composite. As high as 260% increase of damping capacity of this composite was observed after adding GTR reinforcement [81].

Sun et al. [82] developed a layered ceramic/CFRP composite 3D printing process to increase the mechanical performance of this composite. They used poly methyl methacrylate (PMMA), carbon fiber reinforced PMMA (Comma) and ZrO_2 for successful 3D printing followed by methyl methacrylate polymerization. It has been found from the study that overall mechanical properties like flexural strength and fracture toughness of the composite highly depend on ceramic content on the composite. Composite with carbon fiber showed better performance than the PMMA in the composite. Ceramic content by 70% volume showed excellent performances such as strength of 658 MPa and fracture toughness of 15.70 MPa $m^{1/2}$ [82].

Kergariou et al. [83] studied the effect of moisture content on AM continuous flax fiber reinforced PLA composites with a fiber content of 30% vol. Porosity of these specimens has been estimated under ethanol and dry condition, which varied 4.32–6% and 2.733.6%, respectively. One of the key findings from this study is that the strength and stiffness of the polymer composite decreased exponentially with the increase in moisture content. Figure 24 shows the matrix–fiber interaction under loading and the condition that lead to fracture. More specifically, shear strength and transverse strength of the composite decreased by 48% and 44% respectively, with the increase in moisture content from 10 to 98%. The interlaminar delamination, debonding, and the crack propagation ways in the composite are shown in Fig. 24 [83].

8 Future Research Scope

In spite of the tremendous benefit of Additive Manufacturing (AM) for manufacturing fiber reinforced polymer composites, some limitations have been reported in the literature, which can be addressed in future research. Some of the inherent problems of 3D printed parts are porosity, staircase effect, geometrical accuracy and surface finish. It is expected to get better mechanical properties in 3D printed parts by engineering reinforcement materials and orientations of reinforcements. However, mechanical properties of AM polymer composites reported currently are notably

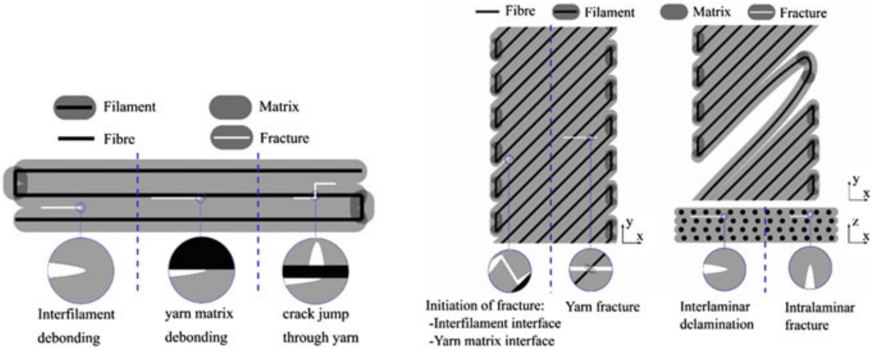


Fig. 24 Schematics of different ways the cracks propagate in the transverse specimens (left side). Fracture evolution due to shear damage (right side) [83]

lower than the convention polymer composites because of its void content. Research may continue to minimize the porosity level in 3D printed parts as well as design various internal structures with high load bearing capacity.

To adopt 3D printing techniques in mainstream manufacturing, existing 3D printing techniques and equipment need to be upgraded to such a level that can overcome the limitation of low productivity, surface finish and tolerance level.

The versatility of materials used for 3D printing of polymer composites is required to increase, which is now limited to mostly thermoplastic polymers with low glass transition temperature and printable viscosity. Future research should focus on 3D printing of other polymers using new and innovative reinforcement materials to improve overall mechanical properties and product performance of 3D printed polymer composites.

To assess failure behavior and forecast the process of failure progression, finite element analysis (FEA) simulation may be used to efficiently reveal the product manufacturing technique. Although there is still a need for more studies on the defect analysis in the additive manufacturing processes, FEA is unquestionably an effective tool for analyzing the structure of polymer composite materials and forecasting failure behavior of composites [84].

9 Conclusion

Additive manufacturing (AM) has made substantial progress with the help of many researchers' restless effort to bring this to light. Despite inherent limitations of 3D printed composites, i.e., anisotropy, porosity, interfacial bonding, geometrical precision, thermal stability, etc., researchers have tried diverse ways to enhance properties of 3D printed composites by using different reinforcements, and printing techniques. To make additive manufacturing of composite at a large scale, extensive research studies need to be carried out. As the global demand for green manufacturing and sustainable manufacturing are increasing, future research on polymer composite should consider recycling, reusing, biodegradability requirement, and use of natural sources of fiber and matrix as a priority. Lightweight polymer composite with load bearing internal structure is now a need for many high-performance applications. As a result, different structures are also explored in 3D printing of polymer composites for good stability and improved mechanical properties. To meet the current need of 3D printed polymer composites and to make AM composites feasible for commercial use, it will need extensive research to explore the undiscovered areas and overcome the limitations of 3D printed composites.

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Chapter 7
Smart Materials Based Additive Manufacturing

Ajit Behera

Abstract Additive Manufacturing (AM) is a constructive industrial manufacturing process termed 3D printing. This is a computer-aided design in which three-dimensional objects are fabricated by applying materials layer-by-layers. Various companies, from the medical to aerospace industries, are using AM. Additive manufacturing is beneficial for creating complex or custom parts. This is true whether you are using it for a new application or replacing an older part that is no longer available. In this era of intelligent technology, AM continues to evolve to keep up with today's demands. 3D printing or AM of time-dependent, stimulus-responsive, predetermined, self-calculated materials is referred to as 4D printing. This chapter describes the additive manufacturing of smart materials with a focus on different given stimulus conditions. In this chapter, we have discussed various applications of smart structures in additive manufacturing.

Keywords Additive manufacturing · Smart materials · 3D printing · Shape memory materials · Shape healing materials · Self-sensing · Self-actuating · Self-diagnosing · Shape-changing

1 Introduction

Additive manufacturing (AM) or 3D printing can produce structures with complex geometries that are impossible with traditional methods. In current decade, 3D printing has evolved to print functional components that can be applied in a wide range of applications, including health monitoring, food processing, electronics, electrochemistry, catalysis, thermal management, aerospace, energy storage, sensors and robotics [1–5]. AM technology has many advantages over traditional manufacturing processes such as great dimensional adaptability, no assembly, no tooling, no

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machining, short lead times, efficient material utilization and the potential to produce functionally graded and multimaterial sections. Overall, 3D printing is proven as an environmentally friendly, more cost-effective, and energy-efficient manufacturing process. Traditional 3D print processes include Stereolithography (SLA), Fuse Deposition Modeling (FDM), Selective Laser Sintering (SLS), and Direct Ink Writing (DIW) [6–10] of the materials. The advent of smart or programmable materials that can be deformed by external stimuli gives interesting new possibilities for 3D printing technology. This combination has created a new field known as 4D printing, in which the fourth dimension is time. This technology was first introduced by Skylar Tibbit in collaboration with Stratasys™ as printed matter programmed to change over time with respect to external stimuli [11]. Many reports on 4D printing focus on the use of smart materials printing, but 4D printing can also be done with "general' materials. These materials can change over time due to predefined stresses created during the printing process by chemical reactions or polymerization between the printed layers. Smart materials require environmental changes such as humidity and heat for conversion, and this environment can detrimentally affect applications. Therefore, stress-driven, controllable, multi-position folding could provide an alternative to achieve transformation without using smart materials. A smart material is a material that responds to changes in its environment, resulting in a change in material properties. Smart materials include shape memory materials and self-healing materials. So far, most reports on 4D printing have focused on the use of SLA, FDM, and DIW technologies. Metamaterials are the type of materials that look like smart materials because of their complex and carefully crafted dimensions, but the material properties themselves need to be more responsive and structural placement is less critical. These self-deforming materials react over time, assembling into new compositions by twisting, bending, contracting and unfolding [12]. They respond to external stimuli such as thermal, electric and magnetic fields, moisture, pH and UV radiation. Combining the dynamic capabilities of smart materials with the complex geometries of the additive manufactured component can be used in different applications, including self-folding packaging, smart textiles, soft robotics, deployable structures, biomedical and aerospace applications.

2 Smart Material Perspective

Materials that function intelligently are referred to as sensitive, intelligent, intelligent, adaptable and multifunctional materials. The general definition of smart materials is the material that responds to environmental stimuli by producing useful reversible effects when exposed to external stimuli such as temperature, electric field, magnetic field, stress, strain, or p^H. Their induced consequences can be color changes, light refraction, stress/strain generation, or changes in shape or volume. Unlike materials, these can sense and respond to changes in the external environment, either by changing their properties, shape, or structural composition. A unanimous definition of a smart material might be one that can change its composition, properties, and dimension when exposed to an external stimulus. Recent advances in material development and 4D printing properties have included them in the AM materials domain. Smart materials are expected to be consistently applied to the manufacture of task-oriented smart structures soon. Predicted responses can give rise to self-sensing, self-actuating, self-healing, self-diagnosing, and shape-changing [13–15].

2.1 Self-actuation Capacity

Smart smart materials can realise multiple actuation mechanisms such as coefficient of thermal expansion, liquid crystalline gel phase transition, thermal conductivity mismatch, and different expansion and expansion ratio of bilayer composite carriers for temporal and spatial actuation. The term “self-actuated” is closely related to shape change and is connected to materials that give large-scale displacements in response to environmental stimuli [16]. Bodaghi et al. [17] have reported a self-acting mechanism through material expansion and contraction in multi-material 4D printing. Planar and tubular structural designs adopted for the T_g-tuned glass and rubber phases of the target SMPs have demonstrated low and high temperature operation [18]. Composites of magnetostrictive and piezoelectric elements, shape memory alloys and electro-rheological materials exhibit this property. Piezoelectric materials are suitable materials that generate an electrical charge when stressed. The technology is in the research stage, and hopefully, self-actuators 4D printed will be from piezoelectric material within a few years.

2.2 Self-healing Capacity

Materials with self-healing powers are sufficient to repair themselves after damage and restore their intrinsic properties, resulting in increased longevity and extended lifespan. Three major healing approaches, such as intrinsic, capsule-based, and vascular, are mainly implemented to bring self-healing capabilities to the 4D print process. A key approach gives the healing of the damage through the reversibility of the material-matrix bond through so-called healing agents introduced in smart material printing to automatically manipulate damages in the print dimension [19]. The incorporation of healing microcapsules is an alternative to achieving self-healing after damage. Healing agents are introduced to the defect area through these transport capsules, which repair the material. Similar to the vasculature of the human body, microchannels have been trained to deliver drugs to relevant sites in the polymer matrix. The presence of self-healing agents in the polymer matrix is likely to influence their properties, making it essential to evaluate the variation and performance of new composites. Recently, some instigation has been carried out to develop the self-healing ability of graphene-based materials. Self-healing coatings based on elastomers and thermosets are implemented as corrosion and deterioration resistance for the material. Powder coating allows these techniques to be used in automotive, civil engineering and aerospace facilities. Product performance, material safety, increased structural durability and fatigue improvement are key attributes of specific self-healing materials for coatings [20].

2.3 Self-diagnose Capacity

Self-diagnostic is an additional early portent feature that can be incorporated into materials. Self-diagnostic material is applied to measure the stressors in stress, strain, etc. Self-diagnosis is the application of self-sensing and most self-diagnosis techniques including sensory elements into materials or structures and fibre optics that have been extensively studied and can sense variables such as stress, strain, pressure, shock, vibration, temperature and corrosion. Self-diagnostic feature is being actively investigated at the Georgia Institute of Technology for fabricating sensors based on the photovitronic effect [21]. Self-diagnostic capabilities are active in research on drug delivery and drug targeting systems for cancer therapy. Stimulus-driven drug delivery mechanisms are more reliable in avoiding drug delivery fluctuations in drug delivery. Near infrared light is a potential stimulus with no medical significance. Thermal photon effects, two-photon absorption and nanoparticle upconverting, are the key mechanisms of intelligent drug delivery. Drug delivery based on photothermal effects has been extensively investigated due to its tunable functionality. Indocyanine green, CNT, and Au-nanomaterials are commonly applied as photothermal agents [22].

2.4 Self-assembly Capacity

The basis of self-assembly is central to 4D printing as it is used interchangeably in inteligent structures. Tibbits reported this capacity by shaking a flask of parts so that the parts self-assembled upon contact. The term self-bending refers to self-assembly mechanisms that use thin sheets fabricated into coiled or cylindrical tubes to exhibit shape-changing effects such as bending, folding, or curling. Sequence of instructions is a key design attribute of self-assembly 4D printing, instructions are a very simple method, and algorithmic description is another part of building complex structures in 3D. It foresaw new types of structures and experimental installations generated by computer code and created through new technologies and possible digital fabrications. It has been shown that any 1, 2 or 3-dimensional geometry can be described by a single sequence or fold line. The folding mechanism and self-assembly are related and active in protein and cell medical research [23].

3 Type of Additive Manufacturing for Smart Materials

Additive manufacturing is defined by the American Society for Testing and Materials (ASTM) as “the joining of materials layer-by-layer to produce an object from 3D model data, as opposed to subtractive manufacturing techniques. According to ASTM/F2921 additive manufacturing can be classified into seven categories, including **material extrusion, binder jetting, material jetting, powder bed fusion, directed energy deposition, film lamination, and vat photopolymerization**. Additive manufacturing has an innate ability to manipulate intelligent and stimulated materials. Again, AM techniques can be roughly divided into **three types**. **The first** is sintering, which involves heating materials without liquefying them to make complex high-resolution objects. Direct metal laser sintering uses metal powders, while selective laser sintering applies a laser to thermoplastic powders to adhere particles. The **second** AM technique melts the material completely. These include direct metal laser sintering, in which a layer of metal powder is melted with a laser, and electron beam melting, in which the powder is melted with a beam of electrons. A **third** widely used technique is stereolithography, which uses a process called photopolymerization [24]. In this process, a photopolymer resin tank is irradiated with a UV laser to create a warp-resistant ceramic part that can withstand extreme temperatures. In terms of input materials, additive manufacturing is divided into solid, liquid and powder technologies. Fused Deposition Modeling specializes in printing solid phase materials that are processed by selective laser sintering, selective laser melting and electron beam selective melting, while liquid materials are printed by stereolithography, direct ink writing and digital light processing. Tailoring appropriate printing patterns has become essential for a wider range of materials with smart settings: There are several additive manufacturing methods are present to print smart materials like Digital Projection Printing (DPP), Selective Laser Sintering (SLS), Selective Laser Melting (SLM), Melting Deposition Modeling (FDM), Inkjet Printing, Stereolithography (SLA), Multi Jet Modeling (MJM), Electron Beam Melting (EBM), Digital Light Processing (DLP) and Polyjet. For the printed part to be considered a 4D print, the part must adapt and alter with respect to time. These categories of materials are known as smart materials and can be further divided into subgroups that include thermodynamic changes in shape memory materials (SMMs), supramolecular changes in self-healing materials, and changes in metamaterial engineering.

3.1 Powder Bed Fusion and Direct Energy Deposition

Several AM techniques have been developed for metal printing so far, but from a 4D printing perspective, the powder bed and directed energy deposition are compelling. SLM is a powder-based printing process that uses a high-energy laser to melt fine powdered materials to create 3D objects layer-by-layer. SLM technology is used in a 4D printing process when smart metallic materials such as SMA are used to laminate high density parts. The production of SMA is not as easy as with conventional materials. For example, NiTi is one of the most popular SMAs. A similar laser melt deposition process to fabricate Cu-based SMA with shape memory behaviour has been performed previously. Selective electron beam melting is another metal printing technique that uses a high-energy electron beam instead of a laser to deposit powder on a moving rake. Porous NiTi implants for bone fixation and minimally invasive surgery have been added to medical applications using EBM based on the assumption that NiTi has a similar stress–strain curve to stainless steel. The DED process featured a multi-axis nozzle arm capable of depositing molten material onto the bed surface. A fundamental understanding of the specific AM technique for target application is prevalent for implementation [25].

The final properties of SLM products generally depend on various process parameters, such as energy density, laser scanning speed and working atmosphere, porosity, transformation temperature and the presence of impurities. Note that the martensitic transformation temperature increases with increasing energy density. The powders used in these studies are typically manufactured by gas atomization from ingots or by mechanical alloying. In addition, a thermal post-treatment was used to control the temperature range for the martensite transformation. In addition to SLM technology, other processes can be referred such as EBM, LENS. EBM technology has high energy density, high scanning speed and high powder bed temperature that allows the martensitic transformation at a higher temperature than the SLM process. Laser Engineered Net Shaping (LENS) method can be used to create nitinol products. A key feature of this work is that the Ni and Ti powder mixture was delivered directly from the nozzle to the laser focus, and the properties of the synthesized nitinol indicate the formation of high quality alloys at specific phase transformation temperatures [26]. The purity of the powder bed fusion synthesized NiTi samples is higher than that of conventional nitinol. A post-treatment heat treatment in an Ar-atmosphere was used to homogenize the microstructure. After heat treating the sample at 1050 °C for 10 h, it was quenched with water. The temperature was chosen to be 100 °C above the melting temperature of the secondary phases that was formed during the LENS. Therefore, it should be noted that all the works use thermal post-treatments to modify and lower the martensitic transformation temperature of the resulting samples. This indicates that the manufacturing of the product by the considered AM method leads to an increase in the final temperature of martensitic transformation of the product from NiTi compared to the base ingot [27].

After identifying the primary reason for the variation in the temperature range of martensite transformation in the SLM process, it is also necessary to find the influence of various SLM parameters. One of the key properties of metal AM processes (including SLM) is energy density. Energy density is the amount of energy dissipated during processing per unit volume of material. This property is used to calculate the thermal energy required to a material during the transition from a powder to a solid state [28]. The energy density is defined according to:

$$E = \frac{P}{Vht} \mathrm{J/mm^2}$$

where P is the power of the source (laser or electron beam) (W), v is scanning speed (mm/s), h is the hatch distance (distance between successive passes of the beam in the same layer) (lm), and t is the thickness of the layer, (lm). It is found that the increase in energy density results increase in transformation temperature. It is observed that a decrease in the hatch distance leads to an increase in energy density. This will increase the transformation temperature of the final sample.

3.2 Fused Deposition Modelling and Direct Ink Drawing

Fused Deposition Modeling (FDM) and Direct Ink Drawing (DIW) are the preferred extrusion-based AM technique for 4D printing. In these processes, material is mechanically extruded through nozzles on the build platform. In a typical FDM process, a printer uses a thermoplastic filament heated to its melting point and extrudes it layer-by-layer to create a 3D structure. Structures printed by FDM may present shape change phenomena due to heating mechanisms. The nozzle can be moved horizontally and the platform moves vertically up and down each time a new layer is applied. In the future, FDM can be used for the AM of graphene-blended polymers. Graphene is a monolayer of carbon atoms arranged in a hexagonal lattice that resembles a chain link fence. When graphene is mixed with SMP, it would make an attractive material with excellent strength and conductivity [29].

3.3 Stereolithography

Stereolithography is wide adopted 3D printing process, especially for SMP additive manufacturing. It is based on the photopolymerization of liquid photopolymers using UV-light. SLA is used for prototype design verification due to its many advantages, such as speed and sophistication. Photopolymers are fabricated from oligomers, monomers and photoinitiators, and UV polyurethane prepolymers are mainly synthesized and printed using SLA technology. Shape memory cycles and folding and unfolding tests were performed to quantitatively and qualitatively evaluate the shape memory performance of SLA-printed structures [30]. The stereolithography process is well suited for printing complex structures using SMPU. SLA printed SMPU structures exhibited fast recovery, excellent shape memory performance, and good dimensional stability followed by reasonable strength. Choong et al. [31] reported a significant performance of full recall shape memory using SLA. Here, A tBA-co-DEGDA photopolymer resin network based on a binary phase change mechanism is used to make the single 4D-printable SMP.

3.4 PolyJet Printing

In this AM process, the material is processed through a nozzle and deposited by consecutive droplets. Polymer metals and ceramics can be printed with this technique. PolyJet technology for 4D printing is made possible by recent regulations on multi-material printing. PolyJet 3D printing with a CAD interface is very similar to traditional inkjet printing. PolyJet printers apply layers of liquid polymer instead of dispensing ink in traditional AM process. Advanced PolyJet technology allows to separate multimaterial liquids to create components formed from various materials. Recent reports have shown that PolyJet printers can be used to accurately print traditional and smart materials [32]. PolyJet technology is most interesting for applications that require the construction of precise, finished, complex and demanding structures. MIT's Self-Assembly Lab collaborates with Stratasys and Autodesk to develop practical modeling and simulation solutions and new printing techniques for these said smart structures [33].

4 Criteria for Printing the Smart Materials

4.1 4D Route and Printing Mechanism

Self-assembly, bi-stability, deformation mismatch, and SME are avenues for 4D printing. Designing and transforming products depending on the specific approaches leads the 4D printing. Self-evolving structures and self-assembly of elements and components are attractive approaches for fabrication of sophisticated smart structures. Swelling rate and different coefficients of thermal expansion or physical changes in smart materials are the driving mechanisms of strain mismatch-based 4D structures [34]. A two-layer beam tends to bend when heated if the layers have different thermal expansion capacities. Bistability means that the imprinted structure exhibits stability at multiple degrees of freedom, leading to reversibility of the structure when exposed to the appropriate stimuli. A fresh 4D technology creates intelligent devices and structures that evolve dynamically over time. Another route is reported by Ding et al. [35] that a temporary dimension is first printed using a Stratasys J750 multi-material printer, then a thermal stimulus is supplied to create a permanent shape. The difference between single-material and multi-material 4D printing depends on the degree of structural variation. In a single material 4D printing process, the degree of change is the response of the smart material while a stimulus is quantitatively applied. The rate of change is the factor that determines how quickly the material component changes configuration when activated. Multi-material 4D printing assesses variations in multiple material components, especially individual variations in dimension and structure. Task-oriented actuation can be fully calculated in the design of modes of release, folding, flexion, compression, extension, torsion, etc., along with the complexity of the fundamental dimension of these required parts.

4.2 Reversibility in 4D Printing

The recoverability of 4D components is relatively unexplored, especially in applications that consist of folding and unfolding cycles involving drying or wetting. Bidirectional 4D printing is shown to be possible using the latest understanding of the SME to improve the design of the 3D printing process. A key element of traditional 4D printing is human interaction during the programming phase during processing. Human interaction can be negated when the programming is appropriately replaced with another stimulus, making this process entirely dependent on external input. SMP showed many possibilities in the reversibility of 4D printing. The print exploits the potential for shape-assisted and reversible transformation characteristic of hybrid hydrogel structures (PEO-PU polymers in UV-curable monomer solution) with important material properties [36]. In the future, the continuous reuse of 4D printed structures will be possible, especially for industrial applications.

4.3 Printing Process

Single-material or multimaterial printing of shape memory non-metallic materials has been fabricated using multiple AM techniques, such as fused deposition Modeling, microextrusion, stereolithography, and PolyJet technology. Choosing the proper impression technique depends highly on the specific SMMs and the desired final configuration. Microextrusion printers use pneumatic or mechanical (piston or screw) metering systems to extrude beads or continuous cells of material. Epoxidized acrylates from renewable soybean oil were solidified into smart compounds capable of supporting the growth of pluripotent mesenchymal stem cells from human bone marrow and laser-printed for biomedical scaffolds. Similarly, polycaprolactone dimethacrylate-based memory tents are manufactured using a UV LED DLP digital printer. For metallic materials, DED, SLM and EBM techniques are suitable for 4D printing.

5 Shape Memory Materials

Shape Memory Materials (SMM) are smart materials that can change dimension or deform with respect to time with environmental stimuli. SMMs include shape memory alloys (SMA), shape memory ceramics (SMC), shape memory polymers (SMP), shape memory composites (SMCo), and shape memory hybrids (SMH). The shape memory effect (SME) of SMA is based on two crystalline structures present in the alloy, the martensite phase (low temperature) and the austenite phase (high temperature). The SMA deforms in the martensite phase, and when the temperature rises to the austenite phase, the structure returns to its original dimension. Like SMA, SMC exhibits hyperelasticity with the capacity to deform and recover under large deformations or a shape memory effect capable of changing predefined states with the help of external stimuli. Some brittle ceramics undergo a martensite transformation and, therefore may experience SME similar to SMA, but one of the main problems with shape memory ceramics is their brittle nature, which is prone to cracking. In the case of SMPs, they react by physical and chemical crosslinking together with temperature transitions such as glass transition temperature (T_g) and melting temperature (T_m). Materials are often processed and molded at temperatures above T_g to create the "original shape", the parts are then cooled down to below their T_g where their shape is deformed and fixed into position [37]. In addition to the commonly used SMMs, SMCo refers to multiphase materials that may contain filler and matrix phases and are combined at the macro level. SMH, on the other hand, refer to two materials joined at the molecular or nanometer level. The transformations indicated by SMH and SMC are related to material components with shape memory capabilities. For example, SMA leads in a polymer matrix undergo a martensitic transformation, while SMH with different polymer phases undergoes physical and chemical crosslinking related to temperature change. SMM is always metastable, transitioning from a transient to a steady state. This altering behaviour is also induced by exposure to switching stimuli.

5.1 Shape Memory Alloys (SMA)

Many reports on SMA describe AM of NiTi, TiNiCu, NiMnGa, CuAlNi and FeMnAlNi alloys using SLS and SLM. SMA is commonly involved with SLS and SLM processes. This is because these 3D printing techniques have traditionally been particularly good at printing metal structures with more substantial properties. Despite its many functional properties, the anomalous behaviour of NiTi shape memory is not very straightforward for several reasons. The main challenges are (1) changing in composition result in a change in transition temperature, (2) SME makes NiTi difficult to machine, and (3) heat treatments (such as annealing) affects phase transformation temperature. There are some problems associated with NiTi print parts produced by the SLM. The printed component reduces the Ni content due to evaporation during the processing due to a lower evaporation temperature of Ni than Ti and the higher phase transformation temperature. This is because Ni has the low evaporation temperature (Ni evaporation temperature = 3186.15 K, Ti evaporation temperature = 3560.15 K) and a high tendency to evaporate [38]. Another explanation is that the heat transfer during the melting process was not uniform due to geometric conditions. As a result, areas normally characterized by poor heat transfer, such as the bottom and edges, have been exposed to high temperatures for long periods. This resulted in increased Ni evaporation and the formation of Ti_2Ni precipitates during solidification. Furthermore, the phase transformation temperature of SLM-NiTi was found to increase by 30 K with decreasing Ni content. The introduction of higher levels of Ni could be a suitable solution for the fabrication of NiTi alloys. The second reason is that Ni-rich NiTi can form Ni-rich secondary phases such as Ni_4Ti_3, Ni_3Ti_2 and Ni_3Ti during high-temperature processing that are formed at temperatures between 200 °C and 700 °C. The order of formation of these deposits corresponds to the order $Ni_4Ti_3 \rightarrow Ni_3Ti_2 \rightarrow Ni_3Ti$ with Ni_4Ti_3 and Ni_3Ti_2. The formation of these phases reduces the nickel content in the matrix. As a result, the matrix composition found more Ti content, as a result the temperature ranges of martensitic transformations shift towards an increase in temperature, which, in turn, proceeding from the dependence that the lower the temperature ranges of martensitic transformations is, the stronger the SME manifests itself, leads to a decrease in the manifestation of SME [39]. To directly address the consequences of the generation of secondary phases in the material, thermal post-treatment methods are used: annealing at different temperatures. The previously formed secondary phase can dissolve during annealing and reduce the temperature range for martensite transformation. Another major problem in conventional NiTi alloy processing is the much higher impurities. This can be solved with the SLM process, where an inert gas is used inside the chamber during fabrication.

Akbari et al. [40] used inkjet printing to create SMA clamps that respond to Joule heating due to electrical current. The group printed and embedded NiTi-wires (0.25 mm in dia) into a “soft” matrix containing a hard phase so that the clamp could move dynamically without breaking. Umedate et al. [41] fabricated a bio-inspired soft robotic model called the Softworm. The movement of the smooth worm was generated by resistive heating in the SMA when an electrical current was applied. Temperature-induced changes in the colour of the straight wires result in large displacements, mimicking muscle tetanus of worms. The body of the worm-shaped design is printed on a Polyjet printer and an SMA coil is threaded through the design to actuate while the tendons are activated. Caputo et al. [42] fabricated 4D printed NiMnGa magnetic SMA with powder bed binder injection. Binder blasting typically produces high porosity parts that can be controlled by particle size distribution and packing density reported a porosity of up to 70.43% for SMA. Thermo-magnetomechanically programmed materials exhibited reversible martensitic phase changes during heating and cooling cycle to control the SME. Dadbakhsh et al. [43] has done NiTi SMA printing using the SLM and studied on the properties of the alloy by varying the power and speed of the laser during printing. SLM processes performed on NiTi powders were classified into low laser parameter (LP) and high laser parameter (HP). LP corresponded to low laser power, slow scan speed, slow heating and cooling speed, while HP corresponded to high laser power, high scanning speed, and fast heating and cooling speed. They found that both sets of parameters produce parts with a density of about 99% and the austenite present at room temperature gave the alloy higher overall strength and pseudoelastic behaviour when printed at high power and high speed. SMA was printed at low power and speed, but exhibited a martensite phase. 4D printing of $Ni_{50.1}Ti_{49.9}$ SMA using SLM was also investigated by Andani et al. [44]. In their study, they investigated the mechanical and SME by varying the porosity and density of the alloy. Dense alloys were found to have higher elastic moduli and higher transformation temperatures than porous alloys. The SMA was subjected to repeated compression tests and showed a 5% recoverable stress and a partial recovery of the hyperelastic response. The porous alloys showed an 86% reduction in Young's modulus while maintaining the SME, indicating that these lightweight 4D-printed structures can be used as biomedical implants, such as bone constructs. SMA's applications include temperature control systems (open and close valves), actuators, biomedical (active implants), soft actuators, and aerospace.

5.2 Shape Memory Polymers

Shape memory polymer (SMP) is ideal for 4D printing applications due to its versatile processing capabilities required for different AM technologies. SMPs are a class of polymeric materials that can be programmed to remember a specific configuration and flip that structure over when exposed to external stimuli. Low cost, light weight, and good resilience are the main features of SMP. Heat, light, electricity, humidity, and magnetism can act as stimuli on SMP structures and produce SME. SMPs can maintain two or more morphologies upon exposure to stimuli. A triple SMP can be enough to memorize two temporary shapes and restore the original shape sequentially when heating. A triple SME can be introduced by incorporating two SMPs with different transition temperatures into the polymer network or by introducing one SMP with a higher transition temperature. A recent experimental study of triplet SMPs printed by FDM devices showed a hyperelastic response at high temperatures and an elastoplastic response at low temperatures over a wide range of strain. A two-component mechanism, a two-state mechanism, and a partial transition mechanism drive the SME of SMP. The shape recovery mechanism depends on the glass transition temperature (T_g) of the specific SMP. This is completely different from SMA. SMPs can be easily adjusted to the environment/application by controlling the crystalline content of the polymer, which can be used to program transition temperatures such as T_g and T_m. T_g is the temperature at which the momentum of the molecule in the glassy state becomes relatively low. A complete SME was observed in thermally activated SMPs when heated above their Tg temperature. On the other hand, the elastic entropy of polymer chains drives the stress recovery mechanism of SMP. Shape recovery depends entirely on the material's capabilities and the application of specific stimuli during specific time intervals [45].

Heat is by far the most widely used stimulus in 4D printing, with temperature differences triggering reactions that promote self-assembly, self-healing, and shape memory in the materials in question. Direct or indirect heating is used in particular light-activated SMP applications. Magnetic, ultrasonic, microwave, or electrical are inherently sensitive to heat, depending on the additives used in the matrix. Physically or chemically cross-linked thermosensitive polymers can be viewed as double, triple, or multiple SMPs. A significant number of such polymers have been reported to recover their original shape, although slight reversibility of temporary and permanent shapes has been demonstrated upon stimulus interaction. The shape memory mechanism operates at working temperatures above and below the T_g or T_m required for mechanical breakdown and subsequent temporary shape formation.

Light is another switching stimulus that can be easily activated due to its intensity, wavelength, and polarization, allowing for touchless control. SMPs containing photosensitive functional groups (such as azobenzene or cinnamic acid) are potential candidates for this class of polymers. Chen et al. [46] prepared a PBS/PLA polymer blend that showed tremendous photothermal effects. Several organic compounds and polymers are highly photon-absorbing and increase their internal temperature due to their high light absorption. High-energy incident photons excite electrons in the particles, followed by electron–electron diffusion, raising the surface temperature. This temperature is lowered by heat transfer between electrons and phonons, followed by heat loss to the surrounding medium due to interphonon interactions. Ge et al. [47] developed a multi-material system to print SMP using microstereolithography. The ink consisted of a methacrylate-based monomer, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide Sudan I (0.05 wt%) and Rhodamine B (1 wt%). The percentages of PEGDMA, BPA, DEGMA, and BMA were refined to adjust the T_g to control fixity at 43 and 56 °C. This allowed the bloom movement of the imprinted flowers to occur in two stages by heating above Tg. However, SLA resins and photopolymers tend to have higher crosslink densities, which means they are more brittle, yielding a design challenge. Gladman et al. [48] demonstrated this behaviour using SMP poly(N-isopropylacrylamide). In this work, a printed flower gets wet and swells and closes. The flowers are printed in a mesh pattern based on simple curved surfaces with 0° and 90° angles made with DIW.

Electroactive polymers (EAP) can drastically change their dimension with an electric field. In electroactive SMPs, Joule heating generates heat when current flows through the polymer domains, initiating the SME. Conductive additives are used to prepare electroactive SMP. Electrically induced mixtures are mainly associated with metals (gold, silver, copper), metal nanoparticles, carbon (graphene, CNT, graphene, bucky gel, soot), conductive coatings, and metal–carbon hybrid fillers. Ionic metal-polymer compounds and dielectric elastomers are types of EAP. SMP containing inductively conductive fillers can achieve certain levels of electrical conductivity, offering an attractive improvement over thermally stimulated SMP. When an SMP containing conductive fillers is exposed to an electrical environment, current flows through the polymer network, raising the core temperature above the transition temperature and springing back into shape. Induction heating induces a shape change in SMP containing ferromagnetic particles achieved by Joule heating. Magnetically embedded SMP have several advantages over direct or electrical heating. For example, magnetic particles limit the Curie temperature and reduce the possibility of overheating. Similarly, contactless heating eliminates the need for power lines. Flexibility in shape formation is possible due to consistent heating, which can be adopted for various geometries. The maximum heating temperature achieved by induction heating, while keeping the magnetic field constant, depends on the surface-to-volume ratio of the embedded magnetic particles and the material. The relationship of the magnetic particles added to the base material, their interaction with each other, their location within the matrix, and their effect on thermal behaviour are still under development. A large volume fraction of magnetic particles leads to a shielding effect between the embedded particles, resulting in a negligible magnetic field effect. Sufficient heating required for ferrite-assisted SMP actuation can be achieved by adding concentrations of 5–10% by volume of particles. Similarly, the incorporated particle size and shape recovery time are directly related to certain limits: the smaller the particle size, the shorter the shape recovery time. There is a critical particle size limit below which recovery times depend on material properties or inherent recovery times [49].

Humidity is one of the main environmental factors of concern to assess the reliability of SMP in humid environments. Adding some nanoparticles through water and solvent evaporation technique can enhance the SME of various polymers. The recovery performance of pure polyvinyl alcohol (PVA) can be improved by adding graphene oxide (GO) mixtures through a solvent evaporation technique, which significantly enhances the shape recovery kinetics of nanocomposites. Yongkang et al. improved the mechanical properties of SMP and the shape recovery reaction with water by mixing citric acid (CA) and GO with hydroxyethylcellulose in different proportions. Studies have shown that various polymers (PVA), polyethylene vinyl acetate (EVA), microcrystalline cellulose (MCC) and polyurethane are suitable for water-sensitive materials. There are reports of using SMP in the form of hydrogels for 4D printing applications. Here, hydrogels are classified as networks of hydrophilic polymer chains, which allows them to retain large amounts of water within the 3D network. Hydrogels are widely used in 4D printing applications due to their excellent processability and ability to change volume based on the environment. Many reports detail the application in DIW and SLA technology for the full range of applications, from biomedical applications to electronic devices. Bakarichi, et al. demonstrate the use of alginate and poly(N-isopropylacrylamide)-IPN in a thermally sensitive actuator to control water flow. The extrusion printed actuators showed a reversible length change from 41 to 49%. Another approach to using hydrogels in 4D printing is multi-material printing [50]. Here, one polymer is printed for structural purposes and a second polymer is printed for responsive purposes i.e. swelling hinges. Two inks can be printed simultaneously to create collapsible structures.

5.3 Shape Memory Ceramic

SME have also been observed in ceramics. In 2013, MIT spearheaded a report on shape memory ceramics. Ceramics are generally considered brittle and cannot be bent, stretched, or distorted without any catastrophic failure. Lai et al. [51] achieved this by modifying the polycrystalline zirconia ceramic with yttria or ceria, resulting in over 7% deformation and the ability to withstand up to 50 cycles. SMC undergoes a similar martensitic transformation, changing the microstructure from tetragonal to monoclinic atomic structure. Lead zirconate titanate-based ceramics have exhibited significant isotropic volumetric shape memory behavior, termed antiferroelectric shape memory compounds. Upon application of a reverse electric field, the previous antiferroelectric shape memory phase can be recovered with a fast recovery speed of 2.5 ms. Phase transitions induced by electric fields make many SMC intelligent actuation applications feasible. Zhang et al. have reported the self-healing SMC using yt-stabilized tetragonal zirconia nanopillars. Liu et al. fabricated an elastomer-derived ceramic EDC using a combination of 40 wt% ZrO nanoplatelets dispersed in PDMS resin. They then threaded either an iron or copper wire through the DIW printed lattice to assist in the folding of their origami structures for 4D printing effect. The printed EDC frameworks underwent a thermal process and chemical etching to remove the leads and leave the ceramic components. SMC applications may be a desirable area for high-temperature actuators and robotics for space exploration and high-temperature MEMS.

5.4 Shape Memory Composites

SMCo consists of at least one SMM (i.e. SMA or SMP). Shape memory bulk metal–glass composites are examples of SMCo. PAC-printed polymorphic sensitive compounds with two hydrothermally energized SMP fibres have been reported in nature [52]. T_g of the Gray 60 blended SMP fibres DM9895 and DM8530 were 380 °C and 570 °C, respectively with the matrix Tango Black having low T_g. Due to the different T_g of the matrix and the two fibers, the composite material can withstand three temporary figures and the permanent configuration is restored by heating above the T_g. The concept of PAC-printed active composites using SMP fibers in an elastomeric matrix was reported in 2013. Polymer active composites are relatively soft composites composed of glassy polymer fibers that reinforce an elastomeric matrix and exhibit a SME. A glass-like polymer fiber acts as a switch during shape transformation. SMPC is widely used in sportswear, judo clothing, orthotics, and medical implants such as cardiovascular stents.

6 Piezoelectric Materials

Piezoelectric actuators and sensors are a well-known and established technology used in various industries, including aerospace, automotive, and non-destructive testing. Global demands for greater efficiency, security, low cost, scalability, less material waste, ease of patterning, and lower manufacturing costs make printing techniques very attractive for the developing piezoelectric devices. Piezoelectric materials convert mechanical energy into electrical energy and vice versa. They offer a wide range of applications and can be used as high-resolution 4D printing for the fabrication of actuators, sensors such as many accelerometers, acoustic imaging, and smart micro/nano devices such as biosensors and energy harvesters. Common applications for piezoelectric materials are barbecue igniters and inkjet printer head actuators. Polyvinylidene fluoride (PVDF) is an essential piezoelectric material used for advanced, high-resolution printing on smart devices. Kim et al. 3D printed fabricate piezoelectric polyvinylidene fluoride (PVDF) polymer films using FDM followed by a corona polarization process. They reported that the β phase of PVDF was transformed by FDM 3D printing. In this case, a high voltage was applied to the intermediate corona poles. Bodkhe et al. used vat light-curing technology to 3D print smart structures with excellent dielectric and piezoelectric properties. Polymer/piezoelectric composites of $BaTiO_3$ nanoparticles and PVDF polymers were printed in filaments ~60 μm in size and stacked to create a ready-to-use, millimeter-scale 3D touch sensor could be detected with a finger touch. Kim's group also used microscale digital projection printing (DPP) to light-cure colloidal suspensions of piezoelectric nanoparticles ($BaTiO_3$, BTO) and polymers, resulting in prefabricated structures in less than two seconds. Under light irradiation, a chemical crosslinking occurs between the polymer and the surface functional groups of the piezoelectric nanoparticles, binding the nanoparticles to the polymeric support. Direct bonding of piezoelectric nanoparticles to a flexible polymeric matrix enhances the piezoelectric performance of composite sheets by cleverly concentrating mechanical stress on the piezoelectric crystals. Kuscer et al. developed a piezoelectric ink composed of $Pb(Zr_{0.53}Ti_{0.47})O_3$(PZT) particles with an average size of 170 nm and stabilized with polyacrylic acid [53]. The ink was cast onto a platinized alumina substrate, dispersed well in a mixture of water and glycerol, and used to fabricate thick films by piezoelectric inkjet printing. It is obserbed that after heat treatment at 500 °C and sintering at 1100 °C, a PZT structure with a local piezoelectric coefficient suitable for technological applications. Another PZT-based piezo ink was developed by Ferrari et al. those have potential applications in the fields of MEMS, sensors, actuators, and energy harvesting are presented. One of these inks consisted of ground PZT powder and a low-temperature polymeric binder. Such development of printed flexible piezoelectric materials is of particular interest as it enables suitable sensitive electronic systems. In particular, electronic skins that can be placed around a robot's body, prosthetic hands, or piezoelectric elements can be manufactured on large-area wafers at less cost than commercial standards.

7 Magnetostrictive, Electrostrictive and Photostrictive Materials

Magnetostrictive materials are generally brittle, which limits the design of complex structures. The development of AM processes, especially laser-based AM, enables the fabrication of complex structures such as lattice structures and topologically optimized components. A related type of transducer material is magnetostrictive material. They are used in various structures, drives and sensor elements of supersonic generators, and micropumps with the advent of MEMS. Printing technology provides a robust and relatively inexpensive tool for the fabrication of magnetostrictive sensors and actuators. Magnetostrictive AM materials include Fe–Co, Fe–Co–V, Fe–Si and Fe–Ga alloys [54]. Previous studies on these materials reported that morphological control of the network structure can select for optimized mechanical properties such as stiffness, stress concentration, and anisotropy. Scheidler and Dapino showed that the stiffness and resonant frequency of the Galfenol/Al 6061 composite alloy can be tuned by adjusting the proportions of each constituent material. Among the magnetostrictive materials, Tb–Dy–Fe (Terfenol-D) alloy and Fe–Ga (Galfenol) alloy are attracting attention due to their excellent magnetostriction of 800–1600 ppm and 400 ppm, respectively. However, terfenol-D is brittle and expensive, and galfenol is less processable. As a result, Yamaura et al. We develop Fe–Co alloys by forging and cold working, and study the effects of alloy composition and heat treatment. Fe–Co alloys have high strength and ductility, which facilitates wire processing and resin encapsulation. The first work on innovative thick film magnetostrictive materials developed by screen printing was done by Ghabham et al. A thick film based on the giant magnetostrictive material Terfenol-D was printed on a 0.25 mm thick 96% alumina substrate. The level of magnetostriction (50 ppm) was lower than that of the bulk material (250 ppm), but better than that of some composite magnetostrictive materials. Karnaushenko et al. has developed innovative inks with magnetic properties displaying Giant Magnetoresistance flakes that can be easily printed on numerous substrates including polymers, ceramics, and even paper. Multiferroic (MF) and magnetoelectric (ME) materials can be obtained by combining magnetic and piezoelectric behaviour. As smart materials that can be activated both magnetically and electrically, they offer greater application flexibility. Based on the pioneering work on the magnetoelectric response of P(VDF-TrFE)$CoFe_2O_4$ composites, it is possible to modify the viscosity of composites and manufacture them by spray-printing. The advantages of spray printing, such as simplicity, industry compatibility, high volume production, and fast time to market, are big advantages compared to the minor drawback of poor mechanical response. We also note that polymer-based printing could also be of great interest in thermoelectric, photovoltaic, and energy storage materials [55].

A dielectric material is a material that does not conduct electricity, but responds to an electric field by showing electrostriction. These materials consist of randomly oriented electrical domains within the material. When the sample is exposed to an electric field, the electric domains become polarized along the electric field. Then, when opposite sides of these domains are charged with opposite charges, they attract each other and contract in the direction of the field according to the Poisson's ratio of the material and stretch in the vertical direction. This effect is secondary. That is, the resulting deformation is proportional to the square of the electric field. In particular, reversing the magnetic field does not change the sign of the strain. 4D printed structures based on PLA/CNT composites were fabricated by FDM. Electroactive SMPC filaments with different CNT contents were prepared, and their electrical, thermal, and shape-memory properties were investigated. Moreover, a series of 2D and 3D printed complex structures were designed and manufactured to realize their shape recovery behaviour under the electrical field. It is found that the resultant structures manifested excellent electroactive shape memory performance. The shape fixation ratio was 100% at room temperature, whereas the shape recovery ratio reached more than 90% under a certain voltage. 4D printing of electrostrictive materials can be done by the materials (such as carbon based composite, metal nanoparticles, polyelectrolyte hydrogel, conductive ink, SMP) using SLM, SLA, DIW, Fused filament fabrication [56].

Photostrictive materials are materials that change dimension when exposed to light, a different and more significant change than heat-related changes induced by light. The optical limitation is found in four main types of materials, including ferroelectric materials, polar and nonpolar semiconductors, and organic polymers. Some photostrictive materials contract, while others expand. The mechanism of this phenomenon varies greatly depending on the material. In ferroelectric materials, photostriction occurs due to a combination of inverse photovoltaic and piezoelectric effects, while in organic polymers it is a phenomenon due to photoisomerization (change in molecular structure due to light) [57]. The effect is usually quantified with a single voltage measurement referred to the photodistortion coefficient. This indicates that the behaviour is isotropic. For ferroelectrics, a photostriction coefficient of 0.45% is considered a very large photostriction response, while for nematic elastomers, photostriction can be as high as 400%. Although the literature on these materials is replete with experimental data showing the voltage produced versus wavelength of light, exposure time, and light intensity, the close geometric relationship between the electrostrictive coefficient and these stimulation properties it is non-existent. There is also a dependence on the depth of light penetration.

8 Metamaterials

Metamaterials were first introduced by Victor Beserago in 1968. These are engineered materials that can achieve properties not found in traditional materials and are labeled as smart materials. Additive manufacturing can fabricate metamaterials with curved structures and patterns that can exhibit unique electromagnetic properties and functions. Metamaterials are based on assemblies of individual unit cells specifically designed to perform functions not inherent to the material. This can be challenging for many AM techniques. Especially since most operate in the 200 to 50 μm range and some metamaterial features may only operate in the nm range [58]. However, recent advances have been made in microstereolithography with resolutions down to 40 nm, and the main applications of metamaterials include sensors, absorbers, acoustic envelopes, and antennas. Chao et al. [59] have reported 3D printing of nylon-based metamaterials using SLS to fabricate lenses with metasurface reflectors. Wagner et al. reported an auxetic metamaterial design for 4D printing of thermosensitive materials using inkjet printing. The combination of metamaterial fabrication with active smart materials allows structures to experience a wide range of movement and deformation while maintaining structural integrity. Most of the research on additive manufacturing of metamaterials have been applied to dynamic mechanical systems.

9 pH-Sensitive Polymers

The control of the pH of liquids in biological, industrial and environmental applications requires certain properties such as stability, compactness, sensitivity and ease of use. To meet these requirements, Yiheng Qin et al. reported on the development of functionalized SWCNTs for pH measurement by inkjet printing. Electrodes printed on the glass substrate showed a reproducible pH sensitivity of 48.1 mV pH^{-1}. This sensitivity value can be increased to 57 ± 0.6 mV pH^{-1} using highly loaded palladium (Pd)-based inks. Therefore, the deposition of Pd thin films from highly concentrated inks (>14% by weight) using an inkjet printing process has been reported [60]. Toluene was used to adjust the surface tension and viscosity of the solution. It can apply a pyrolysis process to adapt a continuous and uniform Pd film to a stable printing ink. A single layer printed Pd film showed a very low resistivity of 2.6 $\mu\Omega\ \mathrm{m}^{-1}$. In order to demonstrate the electrochemical pH measurement capability, the surface of the printed Pd film was oxidized for the conversion of ions to electrons, leaving a lower layer for electronic conduction. Both developed the inkjet printing method used by Qin et al. pH electrodes with sensing capabilities offer a cost-effective alternative to electrochemical control systems and devices. So Wang et al. presented a formulation of pH-sensitive Pd catalyst ink for selective electrodeless deposition of copper on a PET substrate based on styrene (St)-co-N, N-dimethyl-dimethylaminoethyl methacrylate nanocomposite catalyst ink [61, 62].

10 Chromogenic-Systems

The inkjet printing of thermochromic conjugated polymers is believed to bring innovative potential applications for temperature sensors. Bora Yun et al. described these problems with respect to the development of a one-component ink system based on conjugated thermochromic polymer for inkjet printing used in QR code images. With good stability and size distribution, single component diacetylene (DA) inks can be successfully applied to substrates such as paper using a simple inkjet printer from an office. Upon irradiation of the diacetylene-printed paper with ultraviolet light, the formation of a polydiacetylene blue (PDA) image was observed, which exhibits a reversible thermochromic transition with precise temperature intervals well suited for QR codes [63]. Lee et al. [64] developed a colour sensor nanocomposite based on ZnO/10,12-pentacosadic acid (PCDA) compounds using inkjet printing technology. ZnO/poly-PCDA compounds exhibit stable and reversible color properties at typical thermochromic transition temperatures, enhancing their potential for biosensing, thermal, and stress device applications.

11 Other Materials

In addition to metals and semiconductors, other pure functional materials, zinc, lithium ion, and ruthenate were used in AM-based prints to achieve high-resolution capabilities. Zinc and lithium are well known metals used in energy storage devices. Advanced printing of these materials could allow better use of the limited 3D space within the device, which could increase energy density. For example, a comb-shaped lithium-ion microbattery with a 3D-printed Li4Ti_5O_{12} anode combined with a LiFePO4 cathode offers high surface energy density and high power density [65]. Apart from Li-ion batteries, Zn–Ag batteries have shown promising results with high specific energy and high power density. For example, Brahm et al. reported a perfectly 2D planar printed Ag–Zn battery. Ho et al. [66] Microbattery electrodes made with alkaline Zn–Ag deposited directly on the substrate using inkjet printing technology and printed electrodes show improved capacity. The effect of ink formulation and electrode shape design on screen-printed electrodes has been reviewed by Saidi et al. [67], investigating on the electrochemical performance of alkaline Zn/ MnO_2 batteries.

12 Summary and Future Prospective

4D printing is a relatively new research area with many challenges. The further development of 3D printing to 4D printing now offers great application potential. Various materials such as SMA, SMP, SMC, SMH are discussed in this chapter, along with aspects of smart materials such as self-activation, self-healing, self-diagnostic, and self-organizing capabilities for 4D printing. Shape memory materials, piezoelectric materials, electrostrictive materials, magnetostrictive materials, photostrictive materials, metamaterials, pH-sensitive polymers, and chromogenic systems has been discussed to develop by the 4D print technology. Along with their criteria, types of additive manufacturing for smart materials were described, such as powder bed fusion and direct energy deposition, fused deposition modelling, stereolithography, and polyethylene jet printing. One of the future applications of 4D printing is overcoming limitations such as technological limitations, material limitations, and design limitations. Printing of smart materials is still in its infancy and all aspects require extensive investigation using different materials, stimuli and mathematical models with 4D printing. This was indeed a dream with traditional engineering methods.

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Chapter 8

Additively Manufactured/3D Printed Batteries and Supercapacitors

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Abstract 3D printing has revolutionized various industries by permitting the manufacture of complex and customized objects with effortlessness. When it hails to batteries and supercapacitors, 3D printing has shown potential in the growth of newfangled and innovative designs. However, the technology is still in its early stages, and significant research and development efforts are underway to harness its full potential. With recent advances and cost reduction, it can transform the manufacturing process to create intricate and complex designs with better implanted functionalities. Further, vital research into the material development and novel design approaches are the need of the hour.

Keywords 3D printing · Batteries · Supercapacitors · Additive manufacturing

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1 Introduction

Climate change is one of the greatest challenges faced by us in the twenty-first century. The earth is warming earlier than at any time in recorded history. Global warming caused by humans reached the 1 °C mark in 2017. In order to save our planet from the devastating effects of global warming, we need to limit the spike in temperatures to an average of 1.5 °C above pre-industrial levels. This requires the world to cut 30 giga tonnes greenhouse gas emissions annually by 2030. Significant technological intervention in this regard to reduce CO_2 emissions and produce clean electricity, stored safely and cost effectively is the need of the hour [1–5].

Electric vehicles are far better for the environment than the present petrol and diesel-based vehicles. Research has shown that they emit fewer greenhouse gases and air pollutants than the conventional vehicles including taking into account their production and electricity generation to keep them running. For example, a pure electric car produces zero CO_2 when driving on the road. If we quantify this for over a year, a single electric car can save an average of 1.5 million grams of CO_2. Imagine all the present-day vehicles being replaced with electric vehicles—his translates into a considerable reduction in air pollution making our towns and cities a better place to live. However, there are quite a few challenges to make it a reality like safety, cost, energy density and capacity which is holding back the widespread adoption of electric vehicles [6–10].

Traditional lithium-ion rechargeable batteries which are widely used in laptops and smartphones has downsides for both people and the planet. The raw material extraction process is a very much labour-intensive process and requires large amounts of resources like energy and water. Proper recycling of the used batteries is also a major concern. Alternatives for conventional batteries have emerged over a period of time out of which Solid State Batteries (SSB) still holds well as a promising technology [10–15]. They are preferred because they improve safety, size and weight. They offer higher energy density when compared with conventional batteries i.e., a solid state battery pack will give same kWh rating of a traditional lithium-ion battery but it will be lighter and smaller in size. But we don’t see much of the world using SSBs at present because of the complex manufacturing process involved in its making.

3D printing technology provides a way to produce and bring SSBs to the market in a cost-effective way. Conventional batteries follow a two-dimensional planar architecture of the electrodes whereas 3D printing electrodes results in creating intricate battery designs by following three-dimensional architecture. This leads us to imagine beyond the conventional design and bring to life the idea of shape-conformable batteries as shown in Fig. 1.

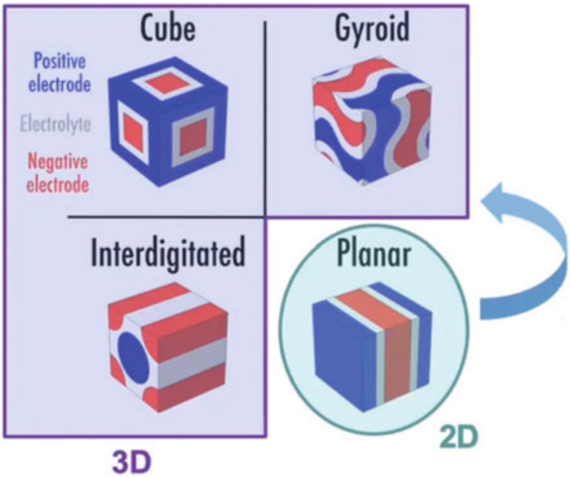
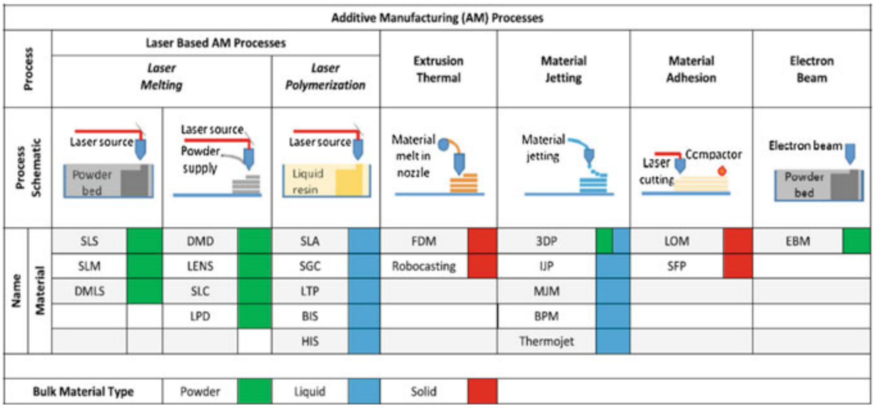


Fig. 1 Graphical representation of two dimensional planar and three-dimensional cube, gyroid and interdigitated battery architectures [16]

2 Overview of 3D Printing Technologies

There are numerous 3D printing technologies that are being developed for various functions and purposes as shown in Fig. 2. According to the ASTM Standard, 3D printing processes are classified into seven categories: powder bed fusion, sheet lamination, vat photo polymerization, material jetting, binding jetting, directed energy deposition, and material extrusion. There are no discussions regarding whether machine or technology performs better because each has its own set of applications. 3D printing technologies are now not restricted to prototype but are hastily being used to create a wide range of items.



Additive Manufacturing (AM) Processes							
Process	Laser Based AM Processes			Extrusion Thermal	Material Jetting	Material Adhesion	Electron Beam
	Laser Melting		*Laser Polymerization*				
Process Schematic	Laser source Powder bed	Laser source Powder supply	Laser source Liquid resin	Material melt in nozzle	Material jetting	Laser cutting Ccmpactor	Electron beam Powder bed
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. 2 Overview of various 3D printing technologies and the corresponding compatible materials [17]

Binder jetting is a rapid prototyping and 3D printing process in which a liquid binding agent is selectively deposited to join powder particles. The binder jetting technology uses jet chemical binder onto the spread powder to form the layer. The application of the binder jetting is would be producing the casting patterns, large-volume products from sand. Binder jetting can print a variety of materials including metals, sands, polymers, hybrid and ceramics. The process of binder jetting is simple, fast and cheap as powder particles are glued together. Lastly, binder jetting also has the ability to print very large products.

Directed energy deposition is a more complex printing process commonly used to repair or add additional material to existing components. Directed energy deposition has the high degree control of grain structure and can produce the good quality of the object. The process of directed energy deposition is similar in principle to material extrusion, but the nozzle not fixed to a specific axis and can move in multiple directions. Furthermore, the process can be used with ceramics, polymers but is typically used with metals and metal-based hybrids, in the form of either wire or powder. The example of this technology is laser deposition and laser engineered net shaping (LENS). Laser deposition is the emerging technology and can be used to produce or repair parts measured in millimetre to meters. Laser deposition technology is gaining attraction in the tooling, transportation, aerospace, and oil and gas sectors because it can provide scalability and the diverse capabilities in the single system.

Material extrusion-based 3D printing technology can be used to print multi-materials and multi-colour printing of plastics, food or living cells. This process has been widely used and the costs are very low. Moreover, this process can build fully functional parts of product Fused deposition modelling (FDM) is the first example of a material extrusion system. FDM was developed in early 1990 and this method uses polymer as the main material. FDM builds parts layer-by-layer from the bottom to the top by heating and extruding thermoplastic filament.

According to ASTM Standards, **material jetting** is a 3D printing process in which drop by drop of build material are selectively deposited. In material jetting, a print head dispenses droplets of a photosensitive material that solidifies, building a part layer-by-layer under ultraviolet (UV) light. At the same time, material jetting creates parts with a very smooth surface finish and high dimensional accuracy. Multi-material printing and a wide range of materials such as polymers, ceramics, composite are available in material jetting.

Powder bed fusion process includes the electron beam melting (EBM), selective laser sintering (SLS) and selective heat sintering (SHS) printing technique. This method uses either an electron beam or laser to melt or fuse the material powder together. The example of the materials used in this process are metals, ceramics, polymers, composite and hybrid. Selective laser sintering (SLS) is the main example of powder-based 3D printing technology. SLS is 3D printing technology that's functionally in fast speed, has high accuracy, and varies surface finish. Selective laser sintering can used to create metal, plastic, and ceramic objects.

According to ASTM definition, **sheet lamination** is the 3D printing process in which sheet of materials are bond together to produce a part of object. The example of 3D printing technology that uses this process are laminated object manufacturing (LOM) and ultrasound additive manufacturing (UAM). The advantages of this process are sheet lamination can do full-colour with lower cost of fabrication and less operational time. Laminated object manufacturing (LOM) is capable to manufacture complicated geometrical parts.

Vat polymerization uses a vat of liquid photopolymer resin, out of which the model is constructed layer by layer. An ultraviolet (UV) light is used to cure or harden the resin where required, whilst a platform moves the object being made downwards after each new layer is cured.

As the process uses liquid to form objects, there is no structural support from the material during the build phase, unlike powder-based methods, where support is given from the unbound material. In this case, support structures will often need to be added. Resins are cured using a process of photo polymerization or UV light, where the light is directed across the surface of the resin with the use of motor-controlled mirrors. Where the resin comes in contact with the light, it cures or hardens [18, 19].

3 Materials Used for 3D Printing Technology

Like any manufacturing process, 3D printing needs high quality materials that meet consistent specifications to build consistent high-quality devices. To ensure this, procedures, requirements, and agreements of material controls are established between the suppliers, purchasers, and end-users of the material. 3D printing technology is capable to produce fully functional parts in a wide range of materials including ceramic, metallic, polymers and their combinations in form of hybrid, composites or functionally graded materials (FGMs).

3.1 Metals

Metal 3D printing technology gain many attentions in aerospace, automobile, medical application and manufacturing industry because the advantages existing by this process. The materials of metal have the excellent physical properties and this material can be used to complex manufacturer from printing human organs to aerospace parts. The examples of this materials are aluminium alloys, cobalt-based alloys, nickel-based alloys, stainless steels, and titanium alloys. Cobalt-based alloy is suitable to use in the 3D printed dental application. This is because, it has high specific stiffness, resilience, high recovery capacity, elongation and heat-treated conditions. Furthermore, 3D printing technology has capability to produce aerospace parts by using nickel base alloys. 3D-printed object produces using nickel base alloys can be used in dangerous environments. This is because, it has high corrosion resistance and the heat temperature can resistant up to 1200 °C. Lastly, 3D printing technology also can print out the object by using titanium alloys. Titanium alloy with have very exclusive properties, such as ductility, good corrosion, oxidation resistance and low density [20–22]. It is used in high stresses and high operating temperatures and high stresses, for example in aerospace components and biomedical industry.

3.2 Polymers

3D printing technologies are widely used for the production of polymer components from prototypes to functional structures with difficult geometries. By using fused deposition modelling (FDM), it can form a 3D printed through the deposition of successive layers of extruded thermoplastic filament, such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polypropylene (PP) or polyethylene (PE) Lately, thermoplastics filaments with higher melting temperatures such as 3D printing polymer materials in liquid state or with low melting point are widely used in 3D printing industry due to their low cost, low weight and processing flexibility. The materials of polymers played important role in biomaterials and medical device products often as inert materials, by contributing implants to the efficient functioning of the devices as well as providing mechanical support in many orthopaedic [23–27].

3.3 Ceramics

Nowadays, 3D printing technology can produce 3D printed object by using ceramics and concrete without large pores or any cracks through optimization of the parameters and setup the good mechanical properties. Ceramic is strong, durable and fire resistant. Due to its fluid state before setting, ceramics can be applied in practically any geometry and shape and very suitable on the creation of future construction and building. According to they said ceramics materials is useful in the dental and aerospace application. The examples of this materials are alumina, bioactive glasses and zirconia. Alumina powder for instance has the potential to be processes by 3D Printing technology. Alumina is an excellent ceramic oxide with a very wide range of applications, including catalyst, adsorbents, microelectronics, chemicals, aerospace industry and another high-technology industry. Alumina has great curing complexity. By using 3D printing technology, complex-shaped alumina parts with has a high density after sintering and also has high green density can be printed.

3.4 Composites

Composite materials with the exceptional versatility, low weight, properties have been revolutionizing high-performance industries. The examples of composite materials are carbon fibres, reinforced polymer composites and glass fibres reinforced polymer composite. Carbon fibre reinforced polymers composite structures are widely used in aerospace industry because of their high specific stiffness, strength, good corrosion resistance and good fatigue performance. At the same time, glass fibres reinforced polymer composites are widely used for various applications in 3D printing application and has great potential applications due to the cost effectiveness and high-performance. Fiberglass have a high thermal conductivity and relatively low coefficient of thermal expansion [28–30].

3.5 Smart Materials

Smart materials are defined as this material have the potential to alter the geometry and shape of object, influence by external condition such as heat and water. The example of 3D printed object produces by using smart materials are self-evolving structure and soft robotics system. Smart materials also can be classified as 4D printing materials. The examples of group smart materials are shape memory alloys and shape memory polymers. Some shape-memory alloys like nickel-titanium can be used in biomedical implants to micro electromechanical devices application. In the production of 3D printed products by using nickel-titanium, transformation temperatures, reproducibility of microstructure and density is the important issue [31].

4 Shape-Conformable Energy Storage Devices

Electrochemical energy storage devices are the key components of portable electronics and electric vehicles. They are designed to store and release electricity through chemical reactions. Rechargeable lithium-ion batteries and supercapacitors are the most common electrochemical energy storage devices. Lithium-ion cells are available in prismatic and cylindrical shape owing to its roll-to-roll manufacturing process. This imposes a limitation to integration in some of the advanced and sophisticated devices.

Electronic casing, a structural outer cover which encapsulates every electronic device forms a dead weight. Fully integrated cells embed functionality in the shape and removes this dead weight. Further, smart watches straps, curved case surfaces, smart glasses frame and implanted medical devices demand flexibility and stretch ability to the battery cells. Hence, shape conformability (adaptation to shape of the device) of energy storage devices opens a realm of opportunities in the design and development of next generation wearables and portable electronic devices as shown in Figs. 3 and 4.

For example, a battery cell can be integrated into the complete frame of the smart glasses. For an electric aircraft, the entire fuselage frame can be made as a battery cell thus eliminating the additional space required in the case of conventional rectangular or cylindrical or prismatic-shaped batteries. Similarly, a battery can be integrated into the structural casing of the cube sat thus aiding in the miniaturization and dead space saving to accommodate more payloads. Further, it can be extrapolated to future applications in space travel like building of extra-terrestrial and lunar/Martian habitats.

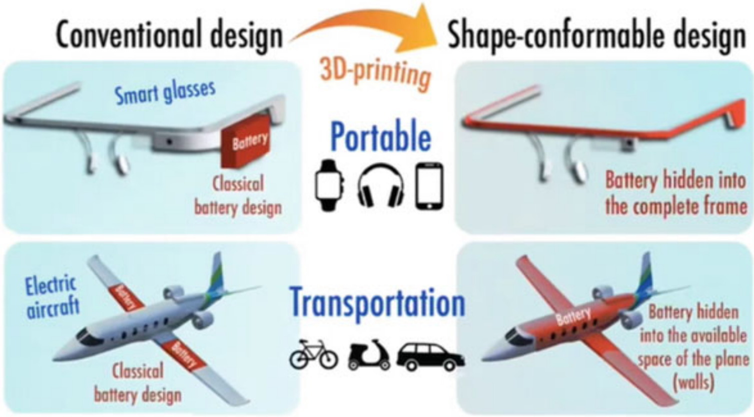


Fig. 3 Futuristic applications of 3D printed shape conformable batteries [16]

Fig. 4 Battery designs [18]

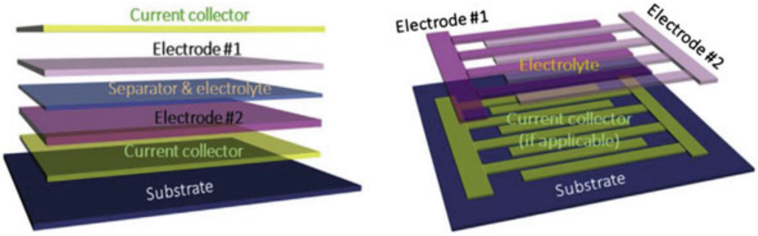
5 Additive Manufacturing of Batteries

The exponential growth in technology has led to the design and development of customized and miniaturized electronics. The power source of these new era devices i.e., a battery also need to be upgraded from functional and aesthetic diversities. Additive manufacturing of the battery's paves way for that with its unique abilities to produce most complex and intricate designs embedded with functionality.

There are three important considerations for additively manufacturing a battery: (a) Design, (b) Material and (c) 3D Printing Technology. To begin with AM process, a digital design of the proposed battery architecture is needed. Engineering Computer Aided Design (CAD) tools and techniques can be used to create a virtual design. This digital 3D model output is then sliced into several 2D horizontal cross sections using a specialized slicing software. The output of the software is a set of commands called a geometric code (G-code) which is then fed to the machine. The 3D printer as per the G-code deposits 2D layers of the thermoplastic material one above the other to fabricate a coherent 3D object.

Design of batteries consists of (a) geometric architecture of its components like electrodes, electrolyte, separator and current collector and (b) the assembly design. With 3D Printing, any complex geometries of electrodes can be fabricated to realize shape conformable design. The assembly of these components can be done by configurations like in-plane or sandwiched designs as seen in Fig. 5. Both configurations have their own pros and cons which affects their electrochemical performance and its application areas. Sandwich configuration is a cost-effective design and is relevant for mass production whereas in-plane design having minimal footprint and enhanced ionic transport is suitable for customized applications like ultrathin film batteries or supercapacitors.

3D Printing technology and material selection is a synergetic process where specific materials are compatible with the certain technologies. The most common technologies used in the fabrication of energy storage devices are material jetting and extrusion. Inkjet printing (IJP) is a material jetting technology in which low viscosity inks are used. Direct ink writing (DIW) and fused deposition modelling (FDM) are extrusion technologies in which DIW uses a liquid feed material whereas FDM



Sandwiched Design **In-plane Design**

Fig. 5 Sandwiched and in-plane configurations of battery assembly [19]

Table 1 Summary of 3D printing technologies, compatible materials and battery performance

Sl. no.	3D printing technology	Materials	Performance	References
1	IJP	Ag NPs	5 mA h cm^{-2}	[1]
		rGo/LTO/NCA	0.35 mA h	[2]
2	DIW	LTO/LFP/SP/PVP	14.5 mA h cm^{-2}	[3]
		LTO/LFP/rGO	1.5 mA h cm^{-2}	[4, 5]
3	FDM	LTO/LMO	3.91 mA h cm^{-3}	[6]
4	SLA	LTO/LFP	500 mA h cm^{-2}	[7]
		NiSn/LMO	2 mA h cm^{-2} mm^{-1}	[8]

uses a solid feed material [32–34]. Table 1 illustrates the various materials and 3D printing methods used in battery fabrication and the corresponding electrochemical performance obtained from them.

For IJP, material properties like viscosity (μ), surface tension (σ) and density (ρ) are related with the nozzle diameter (d) using a non-dimensional parameter called Ohnesorge number denoted by Z. The mathematical expression is $Z = \sqrt{\rho\sigma d}/\mu$. Ink compositions with 1 <Z> 10 are generally expected to produce stable droplets. For DIW, the inks must show shear thinning behaviour with high stress and storage modulus. This allows it to retain the shape of the extruded material during deposition. Along with it, the inks must solidify rapidly and have sufficient mechanical stiffness to support subsequent layers. FDM uses thermoplastic materials like poly lactic acid (PLA) and acrylonitrile butadiene styrene (ABS) in which the solidification of each layer is based on crystallization and chain entanglement of the polymer.

6 Additive Manufacturing of Supercapacitors

Supercapacitors are attractive energy storage devices because of their huge electrical capacitance. Ultracapacitor and electrochemical double layer capacitor are some other names of the same device. The manufacturing of supercapacitors is difficult due to many different types of materials used. Table 2 illustrates the 3D printing technologies used to produce supercapacitors along with material and the corresponding performance [35–37].

At present, there is still place for better understanding of the involved processes and contribution to the existing knowledge of supercapacitor manufacturing technology.

Table 2 Summary of 3D printing technologies, compatible materials and supercapacitor performance

Sl. no.	3D printing technology	Materials	Performance	Reference
1	IJP	PANI-GP	864 F g^{-1}	[9]
		rGO	0.1 mF cm^{-2}	[10]
2	DIW	PANI/GO	1329 mF cm^{-2}	[11]
3	FDM	PLA/graphene	485 μF g^{-1}	[12]
		ABS/CB	12 μF cm^{-2}	[13]
4	SLA	Polymer/NiP/rGO	250 mF cm^{-2}	[14]
		Pyrolysed polymer Ag NWs	0.206 mF cm^{-2}	[15]

7 Conclusions and Outlook

The evolution of new era electronic devices requires a great flexibility in design as well as functionality of present-day energy storage devices. 3D Printing technology has a lot of potential in this regard to manufacture customized and miniaturized electronics batteries and supercapacitors. With recent advances and cost reduction, it can revolutionize the manufacturing process to create intricate and complex designs with better embedded functionalities. Further, fundamental research into the material development and novel design approaches are the need of the hour.

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Chapter 9
Additively Manufactured Electrochemical and Biosensors

Vinayak Adimule, Nidhi Manhas, and Santosh Nandi

Abstract The present chapter describes biosensor device properties and electro analytical methods involved in the development of environmentally sustainable hybrid polymers doped with silver nanowires (Ag NW) nano graphite, conductive polymer composites, graphene, nonporous metals, and carbon nanotubes for the biosensor's applications. The hybrid polymers doped with Ag NW showed bio compatibility, neutral adhesion and the formulated ink was used for the strain responsive biosensors. The nano graphite incorporated for the redox electrodes which are further used for the effective detection of Pb (II) and Cd (II) elements. However, electrochemical performances of conductive polymers showed decrease in the peak current with increase in the electrode potential leading to water ingress and used for the application of additive manufacturing (AM) where water is in contact with the AM process. The electrochemical biosensors used with graphene, carbon nanotubes and porous metals in presence of biomarkers with their challenges in the AM process discussed in detail.

Keywords Graphitic carbon · Conductive polymer inks · Biosensors · Electro analytical techniques · Physiochemical characteristics · Synthesis

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1 Introduction

The efficient detection of the analyte using electrochemical sensors has the advantages due to their rapid sensitivity, high selectivity, and sensitivity [1]. However, electrochemical sensors are very useful instrument for the detection of varieties of the species due to their low cost, potable, miniaturized devices, robust method of analysis [2]. Biological recognition of the species like nucleic acids, enzymes, etc. can be efficiently carried out using electrochemical sensors. The quantitative, qualitative information about the biological receptors can be efficiently carried out using biosensors. The bio electrochemical devices find applications in the field of health care [3], environmental monitoring [4], biological analysis [5] etc. Biosensors can be broadly classified into 2 categories, affinity sensors and bio catalytic sensors. Selective interaction between the analyte and biological species will be carried out in affinity sensors whereas bio catalytic sensors enzymes, nucleic acids, tissue which produces target interaction with the biological receptors during the electro active process [6]. The first developed biosensor consists of oxygen membrane acting as electrodes which have thin layer of GO_x entrapped into the surface of the membrane. The Clark and Lyons [7] has designed the electrode and decrease in the oxygen content is directly proportional to the concentration of enzyme catalysed β-D glucose [8]. Verities of commercial biosensors are used for the determination of small molecules such as lactose, uric acid, lactone etc. and in majority is covered by the glucose biosensors [9]. Graphene oxide (GO_x) has the advantages of low cost, high selectivity and sensitivity which makes it promising candidate for the development of biosensors [10]. The biosensors generally work on the immobilization of enzymes on the electrode surface (first and second generation). GO_x has active centres (13–18 Å) and the mediators will help in transfer of the electrons from the electrode surface [11]. Commercially available sensors essentially consist of customized designs which has low cost, robustness, adopt for the additional factors etc. [12]. For the detection of nucleic acids and proteins (larger biomolecules) faces larger and significant challenges which include electrode fouling, lack of sensitivity, adsorption of biological receptors, range of concentrations etc. [13].

In the present chapter author described the synthesis of hybrid nanocomposites and their characterization, design, fabrication of strain response biosensors, electrochemical and biosensors properties of mesoporous C-based electrodes, graphene, CNTs, Nano porous metal electrodes using additive manufacturing has been discussed in detail.

2 Experimental

2.1 Synthesis of Hybrid Polymers with Ag NW and Their Physiochemical Characterization

The hybrid polymers such as ω-pentadecalactone (LDP) and ε-decalactone (LD) acting as co-polymers were synthesized as per the procedure reported in the literature [14]. In the typical synthesis involved in taking 30:70 ratio of LDP and LD mixtures in a conducting flak immersed in oil bath having N_2 atmosphere. Catalyst Triphenyl bismuth was used in small amounts and the polymerization process carried out for 6 days. The product was dissolved in chloroform, and precipitated by adding methanol, dried at 150 °C for 2 h. To the above obtained copolymer, Ag NWs were dispersed in chloroform solvent (1–3%). The polymers were characterized by ^{1}H-NMR, ^{13}C-NMR, XRD, TGA, DSC analytical methods.

The physiochemical characterization of the hybrid LDP/LD polymers supported with Ag NWs carried out using following instruments and methods.

a. Electrochemical measurements carried out in three electrode system (PAR STAT-2273), glassy carbon electrode and Ag/AgCl as reference electrode. The thin layer of LDP/AgNWs coated on the glassy electrode and CV was measured in 0.1 M KCl solution. The potential range of −0.8 V to 1.0 V maintained at the rate of 100 mV/s. The following equation was used to validate the obtained results. EIS (electrochemical Impedance spectra) recorded in 0.1 M KCl solution in the frequency range of 0.1 Hz to 100 kHz. The EIS results presented in the form of Bode plots. Spectrum analyser (1.0, EIS) [15] used for the analysis of the obtained results. The capacitance (C) can be calculated using the below equation.
b. Viscoelastic Properties were evaluated using dynamic rheological testing (Anton Parr MCR 302). 10 mm, 1 mm distance parallel plates were used and strain rate measured 0.1 to 100% at 1 Hz at constant temperature. The storage modulus over the range of applied strain were determined [16].

3 Results and Discussions

3.1 Design, Fabrication, and *in Vitro* Analysis of Strain Response Biosensors

With the increase in the complexity, the electrode geometries were designed with the help of computer aided designs (CAD). Using Bio scaffolder 3.2 the obtained results were divided standard triangular language (STL) with specific width of 150 μm using AM process, and maintain the ASTM 52,910:2018 standard guidelines the biosensor was constructed. Thin filaments of LDP/AgNWs undercoated over the base material in order to enable 3D printing process using 150 μm nozzle tip. The flexible thermonox substrates are obtained by the optimization of the printing parameters in the instruments. For ideal 3D printing parameters which includes, print velocity of 5 mm/s, 75 kPa pressure and temperature at 37 °C. THF solvent was used for the printing process and can be evaporated quickly after the deposition. The microstructure was characterized using 10X/20X magnification system (EVOS XL core imaging system) the integration of LDP and Ag NWs in the nano composite was analysed using image j software. SEM images were collected in order to understand the microstructure, length of nano-fibres, diameter of the nanocomposites (Hitachi S-400, Japan).

In vitro biosensor properties of the LDP/AgNW studied using Cell scale MCT6 apparatus. The electrochemical resistance change was determined using Princeton model 2273 and power suit software. The bonding wires were developed using Ag epoxy material over the surface of the LDP/AgNW. Three biosensor samples were clamped over the apparatus (actuation device) and surface was exposed to solution containing phosphate buffer at temperature of 37 °C. A60 strain actuators used with 200 N loading capacities, frequency of 0.5 Hz and at 5% strain [17]. Using potentiostat with sinusoidal frequency of 1 kHz, at 1 V. In order to obtain the stability of the biosensor devices, the impedance was collected at 21 days.

3.2 Electrochemical Properties of Nano Graphite

The electrochemical applications of the nano graphite in the AM process involves mechanistically derivatives as reported in the sensing applications [18]. Figure 1 represents the CV curves for the ammonium iron (II) sulphate located on the electrode surface which is generally sensitive to oxygen molecule [19]. The similar electrode systems were developed by Chen et al. [20] and Cumba et al. [21]. In their study, they reported that peak separation increases with increase in the number of oxygenated groups [22]. In the AM process, surface oxygen species analysed in CV with voltage window of ~1.0 V. The peak separation observed is similar to the peak separation of O1s group in the XPS (X-ray photoelectron spectroscopy). For lowed oxygenated groups the peak separation is similar to the reported literature [19]. The Potential usability of the electrode is the determination of Pb (II) and Cd (II) ions in the additive manufacturing process.

Figure 1 depicts the typical square wave and stripping behaviour of the CV curves which are obtained by using AM process for the detection of Pb (II) and Cd (II) ions. In order to increase the sensing characteristics of the electrode, the surface area was structured like honey comb and the analysis of the CV profiles (I_p Vs concentration of the analyte) is linear for the detection of Pb (II) and Cd (II) ions. Recently electrochemically modified AM processed electrodes with potentials between 0 to -1.8 V exhibiting effective sensitivity towards Pb (II) and Cd (II) ions. The previous literature reports suggest the lowest detection limits of Cd (II) and Pb (II) ions by using 3 mm graphitic electrode were found to be 2.0 and 2.2 μg/L while the outer sphere

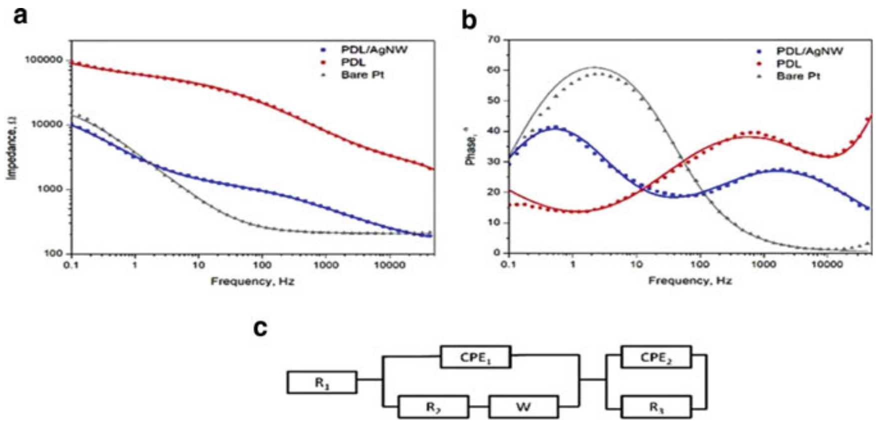

Fig.1 Electrochemical characterisation of PDL and PDL/AgNW. EIS analysis in the form of Bode plots of impedance modulus versus frequency **a** and phase angle versus frequency **b** for PDL and PDL/AgNW, as well as a Pt coated glass electrode; dots represent experimental data, while lines represent simulated results. Equivalent circuit model used for the fitting of the data collected for PDL and PDL/AgNW **c**

redox electrode show 10^{-3} cm/s the difference clearly indicate that the detection limit is much below the limit reported in the previous literature [23].

3.3 Nano Porous Metal Electrodes (NMEs) in Additive Manufacturing (3-D Printing)

Commonly NMEs contain high mechanical resistance, high conductivity, large surface area, and bio continuous structures [24]. Range of metals like Cu, Ag, Pd were used for the MFG of NMEs while, porous Ag NPs find more applications due to their chemical stability, ease of MFG and biocompatibility [25]. The Au NPs size can be tuned to 5–2 nm [26]. The electrode possesses, high surface to volume ratio, high catalytic activity, thermal stability, permeability etc. [27]. The electrodes used in the detection of various substrates in bio catalysis [28], biosensors [29], immune sensors [30], super capacitors [31] etc. Different methods employed for tuning the porous Au NPs. Recently NMEs fabricated using 0.5 N H_2SO_4, via electro analytical reduction having pore size of 40–50 nm [32]. The use of Au NPs avoids the corrosive chemicals and are potentially employed in the glucose oxidase enzymatic biosensors for the effective detection of H_2O_2. Using colloidal crystals, the pore size and the geometry of the Au based NMEs can be controlled. Szamocki et al. [33] reported the use of Au NMEs in the detection of glucose using glucose dehydrogenase via electrochemical method having enhanced detection levels and superior performance [34]. Chemical de alloying is an alternative approach for the NMEs. Different de alloying substances were used such as Au–Zn [35], Au–Ni [36], Au–Si [37] etc.

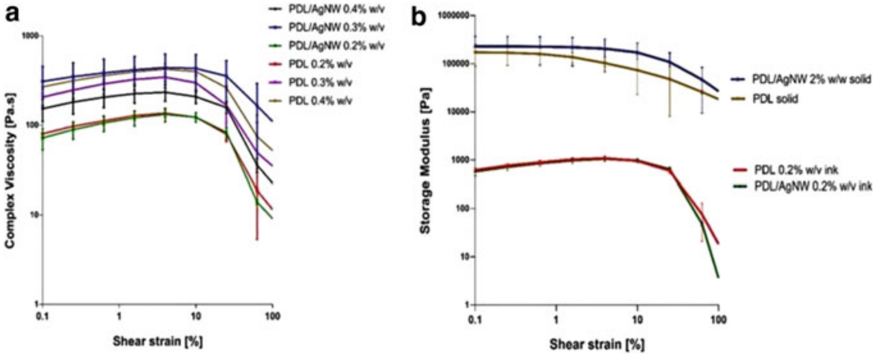

Fig. 2 Rheological behaviour of pristine PDL and PDL/AgNW inks and materials. The viscoelastic properties of PDL and PDL/AgNW composites (**a**), The storage modulus of the of inks and solid polymers was assessed as a function of shear strain (**b**)

Figure 2 shows the schematic alloying of $Ag_{70}Au_{30}$, $Ag_{50}Au_{50}$, Ag_{35} Au_{35} were displayed. On the other hand, wearable sensors play major role in the glucose and other biomarkers monitoring systems such as saliva, intestinal fluids etc. Matharu et al. reported the different pore of Au electrodes obtained via de alloying for the effective investigation of DNA alloying in presence of bio fouling fluids [38]. Electrodes efficiency can be increases with Au NPs of size 20–30 nm using bio fouling fluids. Since the Au is expensive the electrodes can be MFG using low-cost metals like Cu, Fe, Ni etc. [25]. NMEs are widely used electrode systems, however, cost of Au, complexity of MFG, limit the research applications [39].

4 Carbon Family of Compounds in Additive Manufacturing

a. Ordered Mesoporous Carbons (OMCs)

OMCs are flexible membrane structures used for the effective diffusion of materials in the electrochemical systems. The properties of OMCs include high surface area, porous structures, high conductivity, and high thermal and chemical stability [40]. OMCs can be synthesized via catalytic activation of C-spheres, carbonization of organic aerogels, which intern possesses high porous structures of OMCs [41]. Hard templating is also the process for the synthesis of OMCs and can be represented in Fig. 3 The majority of the biosensor's construction mainly dependent on the CMK-1 and CMK-3 biomolecules [42]. In ordered to develop OMCs with low cost, avoiding multi step and controlled pore size, self-assembling of C-spheres and co catalyst as surfactant were used as shown in Fig. 4 [43]. Recent developments include, synthesis of OMCs with large porous and graphite walls [44]. for the construction of glucose biosensors with monolithic electrode matrix using 3D porous graphitic C-nano spheres [45]. In common OMCs are powdered materials and to improve the mechanical properties the use of effective binders required in the modifications of the biosensors. The limitations of the OMCs are high surface volume, ordered mesoporous structures, and the development of alternate materials which can effectively replace the conventional graphene and CNTs.

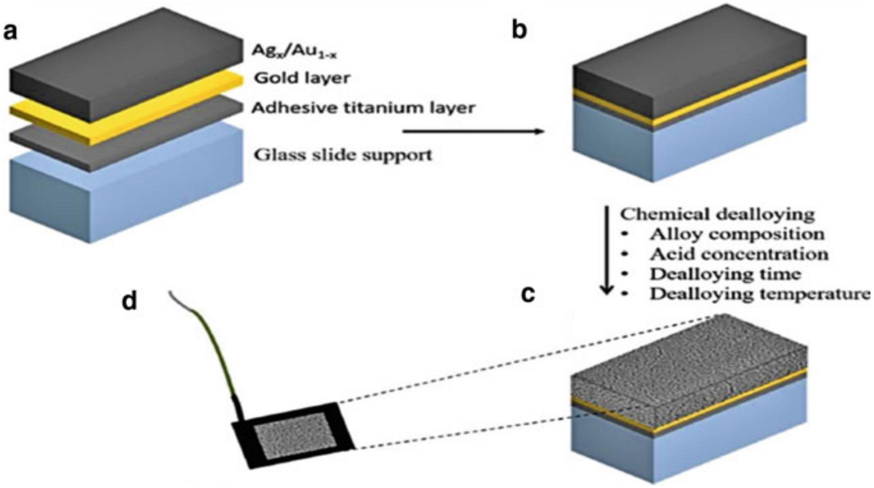

Fig. 3 Schematic representation of the manufacture of nonporous gold (NPG) electrodes with **a** different layers and thicknesses, **b** sputtered glass sheet prior to etching, **c** formation of nanopores after etching, and **d** the completed NPG electrode.

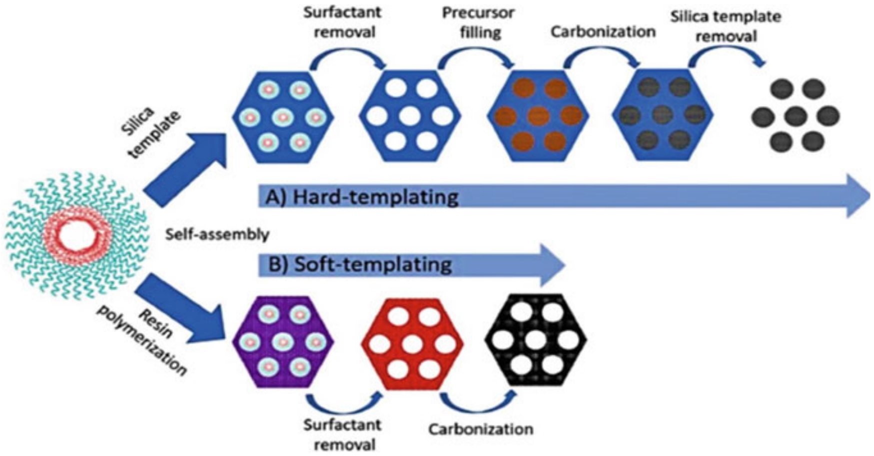

Fig. 4 Two typical methods for the preparation of ordered mesoporous carbon materials: **a** the nano casting strategy from mesoporous silica hard templates and **b** the direct synthesis from block copolymer soft templates. Adapted from

b. Carbon Nanotubes (CNTs)

CNTs can be obtained by rolling graphene sheets having varying diameter and length. Due to their high surface area, high conductivity, chemical and thermal stability, CNTs can be used as transducers and biosensors [46]. CNTs can be commonly divided into 2 types, single walled CNTs (SWCNTs) and multi walled CNTs (MWCNTs). Different synthetic methods are adopted for the MFG of graphene, in common chemical vapour deposition (CVD), different metals like Fe, Cu, Co, Mn can be incorporated into graphene by laser ablation and was reported by Smalley and co-workers [47]. The high-cost method is arc discharge [48]. The interaction between enzymes and CNTs are weak due to non-functionalization of immobilization. It can be increased by the deposition of NPs and polymers. Recently Paolo et al. developed 2-aminoanthracene diazonium salts over the SWCNTs which are placed over FDH which showed high sensitivity and stability [49]. GO_x was immobilized over the SWCNTs for the development of glucose biosensors which can effectively detect the glucose in less than 5 s of response time [50]. A modified Pt-electrodes with rGO/Au NPs/CNTs were used for the detection of lactase. However, toxic effects were rendered as a deposition of metals over the CNTs. The CNTs are tested for wide range of sensors such as DNA [51], immune sensors [52], proteins [53] etc. The limitations include the development of nontoxic, biocompatible, high thermal stability and electronic properties of CNT based biosensors.

c. Graphene

Graphene is an interesting material with flat shape, sp^2 hybridized C atoms, with high surface area, electrical, thermal conductivity [54]. The π electrons are responsible for the electrical conductivity in graphene. The synthesis of graphene involves, Hummer's method [55] in which strong oxidizing agents yield GO (graphene oxide) with the formation of non-conducting hydrophilic C-atoms. The GO produced can be used for the immobilization of biomolecules. Liu et al. [56] reported the immobilization of –COOH, $–NH_2$ groups on the surface of GO and GO_x for the construction of glucose biosensors. In order to prepare the nanocomposite films, a negatively charged GO_x can be used over the chitosan–ferrocene molecules for the construction of biosensors [57]. Owing to the lack of functional groups on the graphene as well as lack of oxygen molecule the pristine graphene can't be used in biosensors [58]. Graphene can be functionalised and electron transfer rate can be increased by doping F, B, P, N, S elements [59]. Electrochemical activity and the accumulation of positive charge density can be increased by way of N-doping to the Graphene molecule which increased the conductivity in solution [60]. Recently poly styrene sulfonate, chitosan, N-doped graphene molecules used as multi-layered structures in construction of biosensors [61]. In order to increase the effective surface area, increase in the π–π interactions, graphene molecule can be added with nanomaterials (chitosan, Au, CNTs) in order to enhance the conductivity and detection [62]. For the detection of cancer antigen 125, using paper based immune sensors Graphene thiophene Au NPs were used [63]. An efficient enzymatic empero metric biosensor were developed by doping graphene, PANI and Au NPs [64]. GO_x modified over

3,4-ethylenedioxythiopphene with Pt NPs retain 97%, of sensitivity after 12 days of usage at room temperature [65]. Graphene can be used as a platform for the construction of biosensors due to its high surface area, ease of functionalization, high conductivity, and the main source of graphene is graphite which is in expensive, real-time monitoring. The limitations include robust preparation of graphene sheets, operational conditions, and its bio compatibility.

5 3D-Printing Technology

The technique of 3D printing or additive manufacturing bring the revolution in the fabrication process as it involves the layered by layer deposition, geometrically complex structure can be fabricated with digital controlled process [66]. The conventional method requires expensive and complex machinery tools, such as milling, drilling etc. [67] and the AM or 3D requires less time, faster rate, and minimizes the waste during the reaction or the process. The specific requirements for the 3D process includes composition, materials, methods and different deposition methods are applied or examined during the AM process which are inkjet printing, selective laser melting, and fused deposition model [68]. The 3D printing involved in the various applications such as electro and catalytic active surfaces, micro needles, fluidic structures, flow channels etc. [69]. AM has promising parameters which makes it to apply and incorporate from the conventional processes, AM enables to overcome equipment and high processing costs, in the preparation of the electrodes. In contrast to other conventional screen printing, AM also reduces the consumption of the materials, formation of waste, deposition of biomolecules, formation of small sized electrodes etc. Figure 5 shows the Au NPs hybridized on the DNA biomolecules for the targeted sequencing. The formed biosensor displayed selectivity of 1–1000 nM. Using non-complimentary DNA sequencing, the hybrid sequencing was analysed. Certain C-based materials commonly used in the AM in order to reduce its costs different methods have been used to optimise the electrochemical performance of the AM electrode system. Kateseli et al. reported the electrochemical performances of C-black/PLA electrode with Nafion membrane having GO_x [70]. A 3D printed graphene/PLA modified electrodes were used for the electrochemical performances of GO_x in glutaraldehyde in presence of solvent DMF [71].

6 Future Perspective

AM process involves completely the digital methods and can able to produce the complex substances. In the field of electro analytical and biosensor methods AM can produce range of complex geometrical structures and electrodes. The AM process has its own limitations which includes, the immobilization of enzymes in the effective

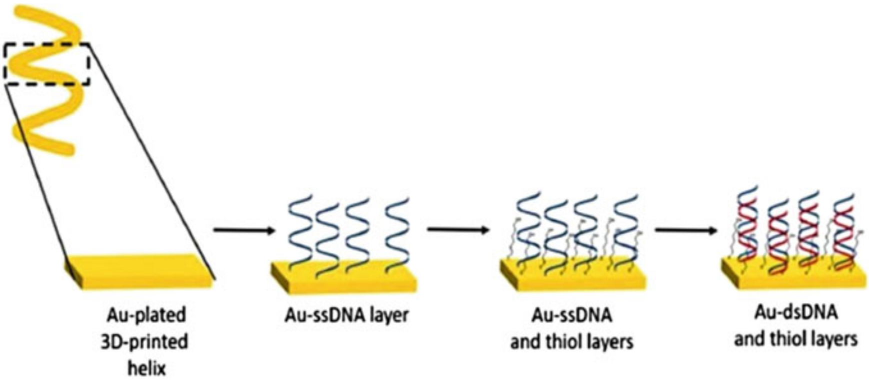

Fig. 5 Schematic representation of the preparation of DNA biosensor. The thiolated DNA was covalently immobilized onto a gold-plated 3D-printed helix electrode. The modified electrode was then incubated with a DNA target, and the electrode was then exposed to methylene blue

detection of substrates using biosensors. Using micro fluids in 3D process will overcome the limitations. Difficulties in the MFG of porous electrodes, high cost of consumables, instruments needed for the AM process, and 3D printing using C-based electrodes are more promising due to their low cost, easily fabricated, and helps in large scale production of biosensors. Further research is required for the development of large-scale 3D printing electrodes with specific substrate detection and their usability in the field of electrochemical and biosensor applications.

7 Conclusion

In the present chapter, additive manufacturing process involved in the hybrid nanocomposites dispersed with Ag NW, graphitic carbon, mesoporous carbon, carbon nanotubes, graphene and conducting polymers were discussed in detail. The synthesis of LDP/LM–Ag NWs, their physiochemical characterization, and procedure for the biosensor constructions were studied. The effect of the various materials in the additive manufacturing process involving electrochemical and biosensor methods discussed in detail.

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Conflict of interest All the authors declare that they do not have any conflict of interest.

Data availability All data generated or analysed in this chapter extracted from open access sources and are included in the published chapter.

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Chapter 10
Additive Manufacturing in Automotive Industries

D. T. Arunkumar, K. G. Basavakumar, P. C. Sharath, and Ashutosh Pattanaik

Abstract One of the most cutting-edge technologies used in the manufacturing industry is additive manufacturing, often known as 3D printing. The additive manufacturing technology uses a layer-by-layer material build-up process to manufacture parts that are created directly from digital models. Metal and polymer components can be swiftly and precisely produced with this manufacturing process. Additionally, it enables flexible manufacturing of customized products without substantially affecting the cost. Due to its attractive features including component design freedom, part complexity, light weight, part consolidation, and design for function, additive manufacturing is particularly suited to the aerospace, automotive, and marine industries. This chapter provides an overview of additive manufacturing methods used in the automotive industry, including material considerations, component design, design limitations, and applications.

Keywords Additive manufacturing in automotive industries · 3D printing techniques · Metallic and polymers components

1 Introduction

Additive manufacturing (AM), more commonly known as three-dimensional (3D) printing or rapid prototyping, is a developing in industry 4.0. AM is a competitive and quickly-evolving technology that enables designers to create speedy prototypes

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as well as complicated designs, which would not have been achievable using traditional subtractive manufacturing procedures. In today's scenario, this novel technology provides significant usage in the automotive industry that could not only expand the range of customization options but also have an impact on how vehicles, parts, and tools are designed and made, opening up a wide range of new business opportunities. The issues that the automotive industry faces today can be addressed with a fresh approach to additive manufacturing. It allows for design flexibility and the development of complicated yet lightweight components [1, 2]. Additionally, this technology is utilised to test, produce, and assemble automotive parts and elements more effectively, optimally, and economically.

Usually companies go iterations method for production of new product or components, but it is eliminated now. Today manufacturer AM is helping to make decision in design stage, quality of the preproduction stage and reducing the additionally extended hours to the market. Maximum design flexibility is provided by AM, which also enables the production of intricate, light, and stiff components. The use of additive manufacturing reduces development and production costs by allowing the creation of components with integrated functionality without the need of tools, and reducing the production cost [3]. Furthermore, the difficulty of directly integrating sensors, batteries, electronics, and micro-electromechanical systems (MEMS) into components and parts, however, has the potential to change production. The diagnosis and resolution of mechanical problems in automobiles can be speed up by the use of additive manufacturing techniques in addition to prototype and design.

AM can enable an automaker to start production months early and save millions of dollars. Example a cylinder head for Ford Motor Company's Eco Boost engines was produced using 3D fast prototyping. Ford was able to design the part, print the sand mould, and cast the metal in just three months, as opposed to the four or five months it would take to cast the part traditionally. The demand for personalization and customization is still high even as globalisation forces automakers toward global platforms and more shared parts and components amongst various automotive models.

1.1 Applications of Emerging Additive Manufacturing to Automotive Parts

Application of additive manufacturing (AM) technologies to make automobile components was constrained by material characteristics, such as surface finishing on aesthetic components or mechanical, thermal, and chemical behaviors under operation.

To enhance materials' mechanical qualities, fibre reinforcements have been incorporated. Recent advancements in carbon fiber-reinforced filament materials have given the FDM technique a new competitive edge. The length of the carbon fibre deposited inside the filament has been addressed in various ways by makers of

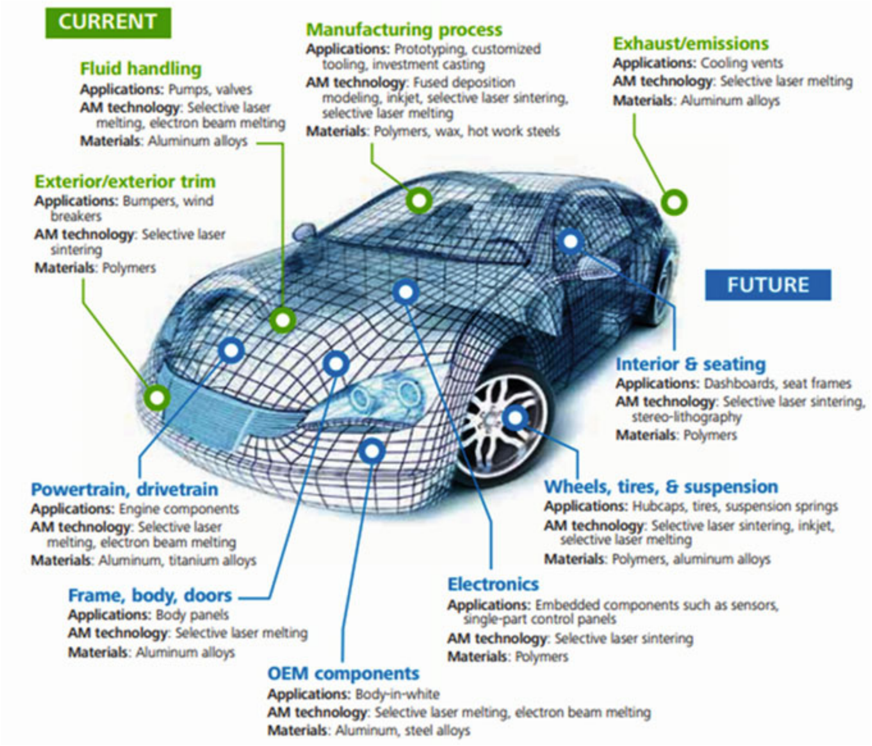


Fig. 1 Current and future application of AM in automotive [4]. [*Source* Deloitte analysis]

AM equipment. Figure 1 shows some of the existing and futuristic uses of additive manufacturing on automobile components.

2 Design for Additive Manufacturing

The design for additive manufacturing (DfAM) method compiles the practices for all-purpose manufacturing processes. Even while AM allows for freeform building, the paradigm change it brought about in manufacturing necessitates additional understanding. The best practices for design for additive manufacturing concentrate on cutting back on resources like raw materials and energy as well as improving the quality of AM components with the use of early numerical studies and process monitoring [5]. In Table 1, the key topics of the DfAM concepts are encapsulated and shown.

Table 1 Design for additive manufacturing key topics to be considered

Resource reduction	Quality enhancement
Weight and cost reduction	Strength enhancement
Building time reduction	Aesthetics enhancement
Handling time reduction	Functionality enhancement

3 Procedure of Additive Manufacturing

3.1 Computer Aided Design (CAD)

The first step in the AM process is creating a digital model. Computer-aided sketching is the method most frequently used to create a digital manufacturing (CAD). There are a wide range of both professional and free CAD systems, including as AutoCAD, Solid Works, and Fusion360, that operate well with additive manufacturing. With the help of advanced tools and 3D scanning, reverse engineering can also be utilised to create a digital model.

3.2 STL (Standard Tessellation Language) Conversion and File Manipulation

The most crucial step in additive manufacturing is the need to transform a CAD model to STL, which makes use of triangles (polygons) to represent the object surface. Here is information on converting a CAD Digital model to an STL file. A slicer Programme is used to convert an STL file into G-code after it has been generated. The NC programming language is called G-code.

The surface geometry of a 3D design is described in an STL file using a network of connected triangles (a process known as tessellation). Then, using a regular 3D printer, you can use this file to manufacture a prototype of any model.

3.3 Printing

Since 3D printing machines can have a large number of tiny and intricate parts, adequate upkeep and calibration are essential to getting the correct prints. The printer is now equipped with the print material as well. The basic material employed in additive manufacturing frequently have limited shelf lives and demand careful treatment. While some methods allow for the recycling of more construction materials, frequent reuse, if not changed frequently, might cause a loss in fabric characteristics.

3.4 Removal of Prints

Some additive manufacturing techniques make it simple to remove prints by simply separating the printed components from the construct platform. In other more commercial 3D printing techniques, removing a print is a highly technical process that involves carefully extracting the print while it remains embedded in the substance or attached to the work piece.

3.5 Post Processing

Due of differences in printer technology, post-processing techniques also vary. Metal parts usually will need to be stress released in an oven using (Stereolithography Apparatus (SLA) however Fused deposition modeling (FDM) parts can be handled immediately after being treated with UV. This is also removed during the post-processing stage for technologies that require support. The majority of 3D printing materials may be sanded, and a variety of post-processing techniques, such as tumble drying, high-pressure air cleaning, polishing, and colouring, are used to get a print ready for usage.

4 Technologies for Additive Manufacturing

4.1 Stereolithography Apparatus

The first of the AM technologies is the Stereolithography Apparatus (SLA), which uses liquid as its basis to create models. Through selective UV laser curing, the models are constructed in layers within a reservoir of liquid thermosetting photosensitive polymer. An ultraviolet (UV) laser beam is used to selectively cure the models as they are built up in layers inside a reservoir of molten thermosetting photosensitive polymer. According to the layer that is currently being created, the laser beam continually tracks and specifically hardens the thin polymer layer [5]. The platform that the model is created on moves down exactly one layer once the layer has been traced. The next layer is then traced once liquid resin has been applied to the sculpture. The layer thickness is in the 50-to 150-m range. Overhang and undercut support ribs are constructed as part of the model and later eliminated during secondary procedures. The platform emerges from the polymer reservoir once the model is finished. The model is removed for post-processing, such as support removal, once the extra polymer has drained away. Additionally, extra curing and surface polishing are required. This method is used for interior and seating components of an automobiles. A variety of photosensitive thermosets are available depending on the application of the SLA technology, but different chemical resins have been developed to closely mimic typical engineering materials like PP (polypropylene), ABS (acrylonitrile/butadiene/styrene), PC (polycarbonate), PE (polyethylene), PMMA (poly methyl methacrylate), nanoparticle resins, elevated temperatures and composite, strong and durable, clear plastics.

4.2 Fused Deposition Modeling (FDM)

In (FDM) Using a heated extrusion nozzle that travels in the X and Y axes, which by convention make up the horizontal plane, fused deposition modelling (FDM) entails feeding a thermoplastic filament (usual thickness 1.75−3 mm). Therefore, the orientation of the Z axis is the vertical plane where the part is constructed. The thermoplastic substance is heated in the extrusion head, which melts and deposits it on a table that travels along the z axis to create the model. Through an extrusion nozzle, the molten thermoplastic is reduced to a fine bead or deposited onto a base material. Each bead is deposited, and then layers of the sculpture are added. Industrial machines typically have layer thicknesses of 125 to 330 m. The liquid thermoplastic material is slightly over its melting temperature when it is deposited, allowing for rapid solidification as the material adheres to earlier layers following extrusion. A variety of materials, including ABS and ABSi (Methyl methacrylate/Acrylonitrile/Butadiene/Styrene/Copolymer), which are useful for observing material flow and light transmission, are utilised in FDM technology. Acrylonitrile Butadiene Styrene (ABS)-ESD7 (Acrylonitrile Butadiene Styrene-Electrostatic Dissipative) that won't cause a static shock or make other materials like powders, dust, and fine particles stick to it; ABS-M30 (biocompatible ABS-M30i); PC; PC/ABC; ULTEM (lightweight and flame-retardant thermoplastic); and PPSF **(Polyphenylsulfone)** [6, 7].

4.3 Binder Jetting

A model is constructed using binder jetting, commonly referred to as inkjet powder printing, within a container that contains either starch or plaster material powder. A measured amount of material powder will be dispersed and compressed by a roller over the building table for each layer. The powered material particles are joined together by a multichannel jetting head using a little amount of liquid adhesive to create the two-dimensional cross section of the product for that layer. After applying the binder, a new layer is swept over the first layer while adding more binder. This process is repeated until the model is finished. Layer thicknesses between 90 and 100 μm are achievable.

4.4 PolyJet Printing

Similar to inkjet document printing, PolyJet printing involves spraying layers of fluid photopolymer onto a build tray, which are then quickly cured by UV light in PolyJet 3D Printers. The material is blasted onto the build area as the head rotates around the print area, curing it with UV light as it passes over the material and hardening it in place. By repeating this procedure, the item is constructed layer by layer. There is no need for post-curing because models are ready to be used and use right away from the 3D printer.

4.5 Selective Laser Sintering (SLS)

The first step in the selective laser sintering (SLS) process is to slice up 3D CAD data into thin cross sections or layers. The SLS additive manufacturing machinery receives the data after that. Next, the machine starts to build the first layer. A CO_2 laser measures the material's cross section after a roller evenly distributes a thin coating of powder material across the powder bed. The surface is scanned by the laser, which heats the material and causes it to fuse. The powder bed gets lowered to make room for the subsequent layer whenever one layer is finished. Unused material is recycled as more material is added from the powder cartridge and rolled out smoothly [8].

Materials utilised in SLS technique include metals like steel, titanium, and alloy combinations; polymers like polyamide (PA) or polystyrene (PS) (neat, glass-filled, or coupled with additional fillers like carbon fibre).

4.6 Electron Beam Melting

EBM is a kind of additive manufacturing used to create metal items. The fundamental distinction between it and selective laser melting (SLM) is that in electron beam melting (EBM), the metal powder is melted using an electron beam in a high vacuum. An automated powder arm adds a fresh layer of material, which is then melted to create the following piece of the model, as each layer is completed. By following the above steps, the item is constructed layer by layer. The build chamber, along with the model and extra material inside, is left to cool when printing is finished. The finished model is then left behind once the scrap is recovered and recycled. Cobalt chromium and different types of titanium can also be used in EBM printers. Because of the vacuum atmosphere and high temperature, EBM may create products similar to those made of wrought material with greater mechanical qualities than cast titanium and cobalt chrome.

4.7 Ion Fusion Formation (IFF)

Using a plasma welding torch to melt metal wire or powder and form an item, Honeywell Aerospace is the only company to use this technique. Metal from a wire or powder feedstock is compelled onto the item by a plasma of hot argon ions. A melt pool is created as the material is fed into the computer-controlled deposition process.

4.8 Digital Part Materialization (DPM)

In 1996, Massachusetts Institute of Technique obtained the exclusive permission to use the Digital Part Materialization technology for metal parts and tooling. DPM builds objects from powdered material one layer at a time using a layering process. An initial CAD file is used, which is then divided into incredibly tiny layers (0.1–0.15 mm). First, a layer of powdered metal is distributed in the build box, and a print head moves across it, depositing liquid binder according to the design for that layer.

5 Driving Factors and Constraints to AM Adoption in the Automotive Sector

Future AM applications in the automobile sector's success will mainly depend on how AM technology advances over the next few years. The potential to influence the trajectory of AM adoption is represented by two drivers and few challenges that have been highlighted.

5.1 Additional Materials that are AM-Compatible

Many different types of materials offer more properties to be incorporated into finished products. Because of the restrictions on the materials that may be used, applications for additive manufacturing have traditionally been limited. AM has not been around long enough to experience such breakthroughs, whereas conventional production today uses a wide array of materials like metals, alloys, and composites [9]. Novel materials have not been widely used in AM because of their high cost. To increase the range of materials available, research has been making steady progress.

In order to improve Mechanical properties [10], new techniques that can combine AM with nanomaterials are currently being developed. In the future, AM might even be utilised to create the body in white for cars due to increases in strength occurring without an increase in weight. Carbon fibre is a worthy example of a sophisticated material. Using traditional methods, carbon fibre is utilised to create lightweight auto parts including fenders, automobile roofs, and windshield frames [11]. With the introduction of the first commercial AM device that can employ carbon fibre, AM is starting to benefit as well.

In addition to new materials, AM acceptance is influenced by new technologies that create current materials more cheaply. Titanium has tremendous appeal in the automobile industry due to its capacity to produce lightweight, high-performance parts. However, widespread use is restricted because to the high cost of the metal powder produced using current techniques, which ranges from $200 to $400 per kilogram [11]. With the potential to save costs by up to 75%, UK-based Metalysis has created a one-step process to generate titanium powder. To employ the affordable titanium powder in AM, Jaguar Land Rover is hoping to collaborate with Metalysis.

5.2 *Enhancing Quality of the Product with AM and Reduced Post Processing*

Usually in automobiles thermal stress or voids are commonly present, with this, parts made using AM technologies occasionally display variability. This causes a decrease in repeatability, which is problematic for high-volume businesses in the automobile sector where quality and dependability are vital. Method for addressing this problem is machine accreditation, in which manufacturers adhere to industry requirements as well as those set forth by AM technology vendors [12]. The other challenge with employing additive manufacturing is that the finished items it produces don't necessarily have the same level of dimensional accuracy as those created using traditional manufacturing techniques.

For example, some studies have found that sand moulds created by additive manufacturing may result in decreased dimensional accuracy in metal casting tools [12]. Another researcher found surface finishes produced by AM methods range in size from 10 to 100 microns, which is often not recognized as being in the high-precision category [13]. The majority of AM-produced components require some sort of post processing, which includes removing unwanted material, wasted material, and increasing surface finish [14, 15].

The quantity of post processing is little for simple pieces. To deploy AM more widely, it might be important to strengthen post processing quality and dependability as the number and complexity of the components grow.

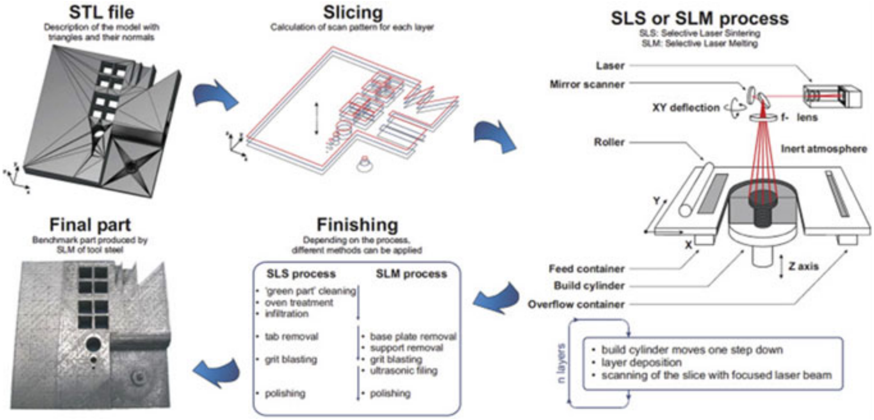
5.3 *Digital Light Processing (DLP)*

Each cross-sectional slice of the object is represented by a light pattern using a Digital Micromirror Device (DMD), which then projects the light pattern onto the photopolymer resin through an imaging lens. The resin hardens and forms the relevant layer as a result of the UV light that is being projected, joining it to the model's surrounding layer. DLP is almost like stamping techniques. After completing the process, washing the remaining resin solution in post processing.

6 Metallic Technologies

6.1 Direct Metal Laser Sintering (DMLS)

Net form pieces are manufactured using the quick prototyping and tooling technique known as direct metal laser sintering (DMLS), which uses lasers. By layer-wise solidifying metal powder layers in areas of the layer matching to the cross-section of the 3-dimensional part in the appropriate layer, complex parts can be created directly from 3D-CAD models. The fundamental idea behind DMLS Technology is to use an electrically powered laser beam to melt down small layers from 20 to 60 µm of metal powder.



6.2 Selective Laser Melting (SLM)

A powerful laser beam and 3D CAD data are combined in the additive manufacturing method known as selective laser melting (SLM) to fuse together thin metallic powders to produce three-dimensional metal objects. A 3D model is first imported into the Programme, which then divides the file into 2D cross sections and delivers them to the printer. Metallic powder is fused together using the power of a powerful CO_2 laser. The same concept as AM occurring during this process as well. The ability to construct thin wall parts to a high resolution, which improves their manufacturing capabilities. The employment of a powerful laser to fuse the material from a powder bed, however, creates numerous processing problems. During processing, increased material vaporization and spatter formation are frequently caused by high heat input.

A general framework has been shown from the analysis of the reproduction or mending of the components. Several parts of a vehicle are included in the AM reconstruction of automotive components, which are often divided into four groups.

- The dashboard, consoles, air vents, mirror, control levers, handles, and switches are all interior features. Process
- Bodywork includes things like the body panels, fenders, bumpers, mirrors, headlights and indicators, grilles, handles, and trim.

7 Challenges of Additive Manufacturing in Automotive Industry

7.1 Inadequate Human Resources

For this relatively new and quickly developing manufacturing technology, humans must be trained in specialized areas of designing and manufacturing. A large professional workforce with expertise in CAD (computer-aided design), AM machine building, maintenance, quality assurance, supply chain management, and fabric preparation is necessary for additive manufacturing to become a reliable and effective process. Not only is it difficult due to the absence of human resources in this area, but also because the available coaching is not standardized, making it difficult to develop a reliable and competent workforce [16]. If AM is to develop as a stand-alone career, the majority of training will need to be structured with dedicated talent development programmers.

7.2 Production Times

The long production delays associated with additive manufacturing are impeding its widespread adoption in the automotive industry, where older, mechanical processes continue to beat it in terms of speed and efficiency. Additionally, three automobiles were produced per second to highlight how expensive manufacturing is worldwide. Strong funding in a quick Researchers from academia, the field of materials science, and industry frequently refer to AM. Although it has become a major focus for searches in recent years, there has only been modest progress made in this area thus far. The low-level manufacturing AM currently providing for a volume-driven sector is no longer feasible for typical business applications.

7.3 Build Dimensions

The small build size of many AM systems is another difficulty for the automotive industry. Larger pieces can be created using 3D printing technology, but they must first be assembled into modules. Currently, these in turn need to be put together or connected using different techniques, such welding. Large-scale additive manufacturing, however, is a significant and developing field of study, and technologies that can accommodate greater build sizes, including Wire Arc Additive Manufacturing (WAAM) and Big Area Additive Manufacturing (BAAM), are currently being actively investigated and developed.

8 Additive Manufacturing's Current Applications

Exhausts and emissions: Typically, this application involves selective laser melting of aluminium alloys to produce cooling vents.

Fluid handling: For melting aluminium alloys, two techniques are used: selective laser melting and electron beam melting. Within the fluid handling system, these methods can be employed to create pumps and valves.

Exterior: Currently, wind breakers and bumpers are made of plastics using selective laser sintering.

Interior and seating's: Dashboards and seat frames might be produced using polymers and the processes of stereo-lithography and selective laser sintering.

Wheels, suspension, and tyres: **To** make suspension springs, tyres, and hubcaps, aluminium alloys and polymers can be worked with the help of selective laser melting, selective laser sintering, and inkjet technology.

Electronics Components: Selective laser sintering can be used on polymers to create a variety of sensitive components, including elements that must be embedded, such sensors, and single-part control panels [17].

Frameworks: It is possible to build body panels, including the structure and doors, using selective laser melting on metal alloys such as aluminium.

Engine Components: When processes like electron beam melting and selective laser melting are applied, various functional elements of the engine can be manufactured from metals like titanium and aluminium [18, 19].

9 Sustainability Analysis

A crucial component of human activity and a crucial concern for human progress is sustainable development. The concept of sustainable development holds that social, economic, and environmental issues should all be handled holistically and concurrently in this process. Many industries, particularly manufacturing, are concerned with sustainability. Sustainable development, according to the World Commission on Environment and Development (WCED), is defined as development that "meets the requirements of the present without jeopardising the ability of future generations to satisfy their own needs". Manufacturing with a focus on sustainability connects its processes to the environment. Today's manufacturing companies take into account profitability, productivity, advancement, and environment protection. The responsible use and preservation of the environment through sustainable methods is known as environmental stewardship.

Many different strategies for incorporating sustainability into industrial processes have been devised and put into practice by businesses. One of these is the "triple bottom line" approach, which John Elkington developed in the middle of the 1990s.

Many companies have adopted the Triple Bottom Line (TBL) concept, which combines the social, environmental, and financial aspects of performance.

10 Additive Manufacturing's Potential for Future Advancement

- Future RP systems will use faster computers, intricate control systems, and better materials to shorten build times.
- By producing quality laser optics and machine controls, part accuracy and surface polish can be enhanced.
- The introduction of non-polymeric materials like metals, ceramics, and composites reveals highly expected advancements in RP. Additionally, the range of items that can be created RP will be greatly expanded by the use of metals and composite materials.

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Chapter 11
Additively Manufactured Medical Implants

Ilker Emin Dağ and Baris Avar

Abstract Technology has greatly advanced due to the internet and digitization, leading to the commercial production of additive manufacturing in the 2010s. This technology allows for the quick and precise creation of needed models, using a variety of materials, easily accessible printer raw supplies, no waste after production, and high production of intricate designs with precision. The digital data can be transferred quickly, and many products can be produced simultaneously in different places. These advantages have led to an increase in production with additive manufacturing. In the biomedical industry, traditional manufacturing methods cause problems with a large number of manufacturing through a single model, particularly with implants and prostheses. With additive manufacturing technology, patient-specific drug formulations, optimum dosage medicines, and patient-specific spinal, dental, hip, craniofacial implants and replacements can be manufactured with high precision. Additionally, tissues and organs can be produced via 3D printing, which helps overcoming issues such as incompatibility and a shortage of suitable donors. In this chapter, several additive manufacturing techniques and implant studies produced by these techniques have been considered in the literature, taking into account all the above aspects.

Keywords Additive manufacturing · Medical implants · 3D printing · Methods

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1 Introduction

According to the FDA, medical implants are defined as instruments or tissues placed inside and on the surface of the human body. Based on this definition, while many prostheses can function as implants instead of defective or lost organs, biomedical materials such as orthopedic, cardiovascular or dental implants also contribute to the healing of diseases or the continuation of vital activities by supporting tissue, skin, bone. While implants can be manufactured from engineering materials such as metal, ceramic, polymer or composite, they can also be produced from body parts such as living tissue, skin, and bone [1]. Pandey et al. categorized all implant groups into three primary categories, including orthopedic, cardiovascular, and other implant applications. In this classification, orthopedic implants are subdivided into reconstructive joint replacement, spinal implants, orthobiologics, and trauma implants. Cardiovascular implants include pacing devices, stents, and structural implants. Otolaryngological, ophthalmic, gastroenterological, gynecological, and pharmacological implants are some examples of subgroups included in other implants [2]. Evaluating a single material property is not enough to describe a specific material desired for so many different implant groups. Achieving excellent biocompatibility is critical in biomedical implant design. The implant materials should not cause an allergic response in living tissue, tissue integration should be complete, and the implant should display compatible function within the implanted region. Researchers have explored various approaches to achieve excellent biocompatibility, including employing various designs, alloys, or materials with different physical, chemical, or biological properties [3]. Recently, the connection between biological characteristics and biocompatibility has been better understood. Biomedical implants must be designed specifically for the illness, damaged tissue, or other condition in which they are going to be applied to avoid implantation failure. Advancing manufacturing technologies aim to create implants that heal quickly and cause no allergic response while keeping production costs low thanks to low energy and raw material consumption [4]. The conventional techniques of manufacturing have the objective of generating economical commodities through the creation of a voluminous quantity of articles possessing identical dimensions, contours, and material composition. Nevertheless, this approach does not hold validity particularly in the case of biomedical grafts, as individual patients necessitate distinct categories and proportions of grafts and prosthetics. If patient-specific implants are not produced, the risk of implantation failure causes many negative situations for patient health. Additive manufacturing technology enables the production of patient-specific biomedical implants and prostheses that are nearly perfect match for the anatomical structure of the individual. This technology eliminates many of the shortcomings of traditional manufacturing processes, including worker faults, high raw material use, and high costs for single products. In recent years, additive manufacturing has allowed for the production of high-precision implants, dental molds, craniofacial-braces implants, and tissue scaffolds for dentistry and bone implantation. Additionally, additive manufacturing techniques show promise in creating biological tissues and organs besides technical

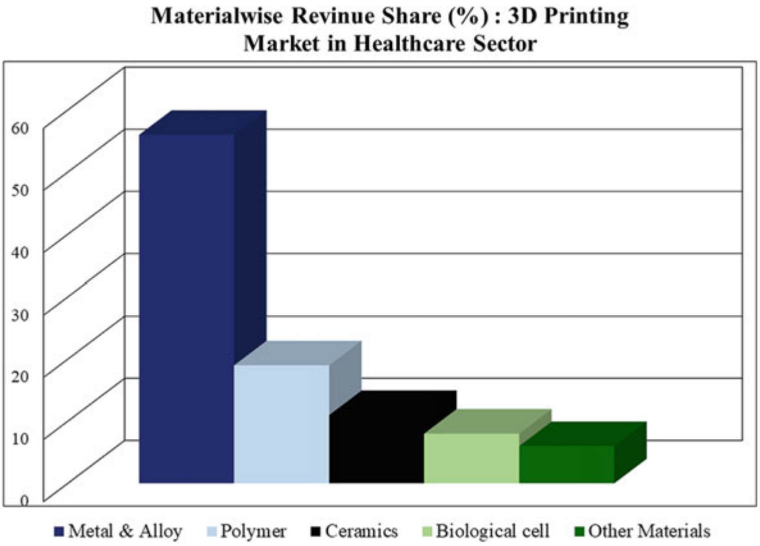

Fig. 1 3D printing healthcare revenue comparison by material type [6]

materials [5]. According to Fig. 1, the category of metals has generated the largest revenue in additive manufacturing for the health industry. It is also anticipated that, by 2027, external devices will represent 12% of the additive manufacturing market in the health sector, with biomedical implants occupying the second largest share [6].

2 Additive Manufacturing Methods

2.1 Definition of Additive Manufacturing

Additive Manufacturing is defined by the American Society for Testing and Materials (ASTM) as "AM is a regenerative process of direct printing physical models from designing software using layer-by-layer fabrication techniques." Additive manufacturing or 3D printing with its widespread use is conducted in many areas such as space and aviation, electronics, industrial products, turbine blades, jewelry, mold manufacturing and biomedical implants. The reasons why it is employed in so many areas include its low cost for customized applications, high model production speed, design flexibility, less material expenditure for the final product, one-stage manufacturability, and constantly developing technology [7]. Nevertheless, there are drawbacks as well, such as slow speed for high-volume manufacturing, the need for post-production surface treatments, and the production capacity being limited by printer settings [8].

Fig. 2 Steps of additive manufacturing process

Additive manufacturing processes vary depending on the area, material properties, shape size, and the number of patterns. Generally, the initial phase of additive manufacturing involves creating 3D model data using computer-aided design (CAD), MRI, CT, or laser scanning, as shown in Fig. 2. These datas are then transformed into a standard triangulation (STL) file so that a slicing software can be used. Free slicing programs like Ultimaker Cura, Prusaslicer, Octoprint, Astroprint, Chitubox, Slic3r, Ideamaker, and Repetier, as well as paid slicing programs like Netfabb and Materialiase Magic, help in creating the STL G file. The manufacturing parameters are determined with a slicing software before producing the models with a 3D printer. The post-processing stage involves the elimination of surface defects on the supports created based on the manufacturing technique. Overall, additive manufacturing has emerged as a promising technology in many fields and is set to revolutionize the production of customized objects that are tailored to individual needs.

2.2 Classification of Additive Manufacturing

More than 50 commercial additive manufacturing systems are available today. Nonetheless, ASTM has basically separated these procedures into seven processes, as shown in Fig. 3 [9]. Among these procedures, binder jetting and powder bed fusion employ powder raw materials, while in material extrusion, a slurry or direct material is deposited on the material via a nozzle or aperture. Furthermore, the photopolymerization process selectively hardens objects using a laser or UV light source, resulting in greater accuracy compared to the vat polymerization technique [10]. The optimum additive manufacturing techniques are chosen for biomedical applications by taking into account the superior physical and chemical qualities needed from the material to be developed, as well as affordability, speed, and the manufacturability of complicated geometries. Given this circumstance, Fig. 3 presents the most popular additive manufacturing techniques for producing biomedical implants, as well as the resulting implants' comprehensive attributes and relevant literature reviews.

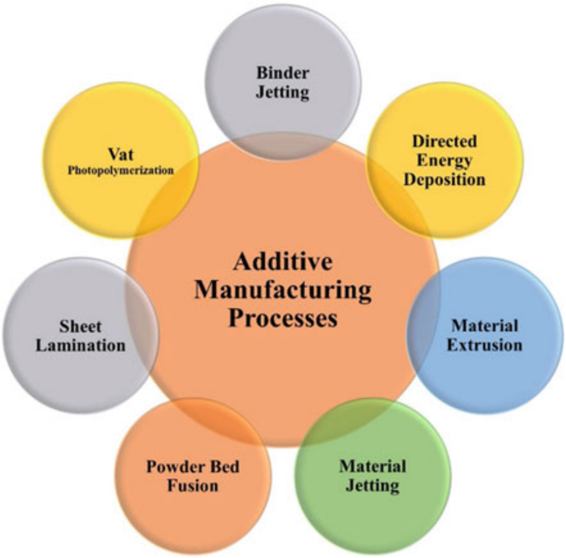

Fig. 3 Additive manufacturing processes according to ASTM F2792-12a standard [9]

3 Literature Review of Additively Manufactured Implants

It is evident that the most widely used additive manufacturing processes for producing implants are selective laser melting, vat photopolymerization, material extrusion, and inkjet printing (binder jetting). This section provides a detailed exploration of the manufacturing techniques, material usage, design and process parameters, as well as the mechanical, biological, and physical characteristics of implants produced through these procedures.

3.1 Binder Jetting Method for Biomedical Implants

A powder bed chamber is used in the binder jetting technique. In accordance with the slicing data, a 2-dimensional layer is produced by selectively spraying binder on the powder bed and rolling the powder for each layer. The platform lowers after each layer by the thickness of layer, and the procedure is then repeated. The manufactured green parts definitely need secondary and tertiary procedures since they are just bonded with a binder and are formed with low power. If debinding and sintering processes are not performed, the manufactured parts cannot be used in most cases due to their low mechanical properties [11]. In comparison to other additive manufacturing techniques, the binder jetting method produces significantly bigger parts and allows for the use of polymer, ceramic, and metal powders in a broad spectrum of materials [12]. The binder jetting technique is a popular method for the development of medical implants in tissue engineering, dentistry, and orthopedic applications, utilizing additive manufacturing. With this technique, a wide range of materials can be produced, as shown in Table 1, which presents the raw materials, production variables, results, and applications for biomedical implants, manufactured using the binder jetting technique. The production of polymer-based implants using this method has been relatively uncommon. In 2002, Lam et al. produced cylindrical scaffolds utilizing powders derived from cornstarch, dextran, and gelatin. Although the mechanical and water-absorption properties of the scaffolds were investigated, the biocompatibility and in vivo characterizations were not analyzed [13]. The binder jetting technique is widely used for fabricating ceramic and ceramic-based composite implants, which occupy a significant space in the biomedical implant industry. Ceramic materials are known for their high temperature phase transitions and high melting points. However, the mechanical properties of traditional porous ceramic materials are not up to the desired standards, and they are vulnerable to cracking, bending, and breaking. Therefore, in the binder jetting process, researchers primarily focus on maintaining the desired part geometry and mechanical properties while also ensuring controlled sintering and appropriate temperature regulation. Using the binder jetting technique as implants, many individuals have studied tricalciumphosphate, hydroxyapatite, calcium sulfate, alumina, porcelain, and many forms of composites, particularly in the bone and dentistry fields [14]. Due to the close cytokichiometric chemistry of hydroxyapatite to bone, Leukers et al. conducted experiments to produce bone scaffolds using HA powders and observed successful propagation of MC3T3-1 cells as well as interaction with HA granules [15]. Similarly, Sheydaeian et al. fabricated porous proximal interphalangeal (PIP) joint implants using a blend of calcium polyphosphate and PVA, resulting in implants with suitable mechanical properties and porosity for in vivo studies [16]. Wu et al. used a mixture of $CaSiO_3$-PVA to manufacture biocompatible and mechanically robust scaffolds, which demonstrated significant bone growth in mouse femoral defects after 4 and 8 weeks [17]. Miyanaji et al. used the binder jetting technique to make porcelain implants for dental applications and optimized the process through the manipulation of printing parameters [18]. Moreover, calcium phosphate implants were produced with high precision for cranial and maxillofacial applications. Personalized implants were produced with high precision. The designs were obtained by converting the CT scan result data into CAD format. Figure 4 depicts both the implants' overall appearance and specific application regions [19]. Again, binder jetting is used to manufacture ceramic-ceramic composite implants with extreme precision. Fielding et al. utilized varying amounts of SiO and zinc oxide to develop ceramic-ceramic composite scaffolds for bone implantation and dentistry using tricalcium phosphate powders. The investigation revealed that adding low levels of SiO_2 and ZnO powders improved the mechanical and biological characteristics of tricalcium phosphate scaffolds [20]. Additionally, in 2014, calcium phosphate-collagen composite scaffolds with suitable biodegradability and mechanical properties were developed for non-load-required bone healing applications. These ceramic-ceramic and calcium phosphate-collagen composite scaffolds offer potential benefits in the field of bone implantation and healing [21].

Table 1 Applications of biomedical implants produced by the binder jetting technique

Material	Aim	Application	Essential findings and details	Ref.
Hydroxyapatite (HA)	To investigate the reproducibility of ceramic scaffolds with specific pore size	Bone tissue engineering scaffold for repairing osseous traumatic problems	HA powder tissue scaffolds were devised effectively with pore sizes reduced to 450 μm and strut thickness of 330 μm. Although the CAD-designed scaffolds were 3% smaller than 3D-printed ones, they shrank between 18 and 20% upon sintering at 1250 °C. The mechanical properties of scaffolds were subsequently evaluated by conducting compression tests on scaffolds with layer thicknesses of 200, 250, and 300 μm. The mechanical properties were comparable to commercially available bovine HA substitutes. The findings suggest that the fabricated scaffolds, created via binder jetting, have potential for use as a bone replacement implant	[24]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Tricalcium phosphate (TCP)	Properly fabricating a patient specific implant for craniofacial defects with a degradable material	Individual cranial and maxillofacial implants	Bone defects on human cadaver skulls were created and analyzed to generate specific implants. The analysis was conducted by producing geometric models using DICOM files. Subsequently, the models were converted into STL files for rapid prototyping. The implants were produced utilizing a binder composed of 20% phosphoric acid (H_3PO_4). While the porosities of the implants ranged from 28 to 35%, they had thermal conductivities (0.294–0.393 W/mK) that were substantially lower compared to titanium implants (21.9 W/mK). As compared to titanium-based implants, manufactured biodegradable implants for craniofacial defects have advantages such as biodegradable structure and lower heat conductivity. Also, the implants were produced with a high degree of precision (200 μm)	[19]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
IPS inline dental porcelain powder	To investigate the effect of some parameters in the binder jetting method for the production of ceramic dental prosthesis	Dental prostheses applications	The impact of variables such as binder ratio, drying time, sintering duration and temperature, heating rate, and powder spreading rate, on the strength and porosity of the material was thoroughly investigated. During sintering, the Z-axis exhibited the most shrinkage. The sintering process carried out at 950 °C resulted in the most significant amount of shrinkage. Although the waiting period had a negligible effect on shrinkage during low-temperature sintering, this trend was more noticeable at 900 °C. Furthermore, compared to the heating rates of 100 and 5000 °C/h, the 500 °C/h rate indicated the highest rate of shrinking. An optimum sintering temperature of 900 °C was identified with a porosity value of 6.5% for a 1-min process. Additionally, the geometric precision was 0.1 mm	[18]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Calcium phosphate (CPP)	Designing and manufacturing anatomically suitable porous small ceramic implant	Proximal interphalangeal (PIP) joint implant	To initiate the design phase, a human phalangeal bone was subjected to CT scanning to generate the necessary DICOM file. The Solidworks CAD software was then used to design, model, and generate STL files for three different resection zones. Finite element analysis was implemented by applying a 50 N force to these models. To manufacture the implants, cylindrical pieces with dimensions of 4 mm diameter and 6 mm height and layer thickness of 175 µm were produced using 90% CPP powders with a grain size of 75–150 µm. These parts were eventually sintered through a three-stage process prior to compression and density testing. The produced materials were found to have a porosity of 77.63% and a strength range of 44.58–18.31 MPa. Even though the designed pieces were successfully fabricated, further in vivo investigations are necessary before considering their application in small joint arthroplasty	[16]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Commercially pure titanium (CP)	Manufacturing low modulus porous titanium implant	Porous dental implants	To create green parts, 325 mesh titanium powder and PVA binder were employed. Subsequently, printed implants underwent a two-hour sintering process at temperatures of 1250, 1300, and 1350 °C. Compression tests and microstructure analyses were performed on the implants, along with in vitro cytotoxicity studies utilizing L-929 fibroblast cells. The dental implant prototypes approximately matched the elastic modulus of natural bone, with ranges situated between 4.8 and 13.2 GPa for various sintering temperatures. It was also established that all implants displayed low toxicity	[25]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Fe and Fe-30Mn	Investigating the possibility of 3D-inkjet printing of Fe-30Mn alloy	Biodegredable bone scaffolds	Iron and manganese powders were mixed for 30 min using a Retsch Pulvarisette P5 planetary ball mill. Parts were produced with a layer thickness of 100 µm. Tensile, cell culture, and electrochemical corrosion tests were conducted for each printed piece. Based on the tensile test outcomes, the materials exhibited mechanical characteristics comparable to bone, and therefore presented adequate mechanical properties for low load applications, such as craniofacial scaffolds. The electrochemical tests demonstrated that the Fe-30 Mn alloy had lower corrosion resistance than pure iron. Additionally, the presence of Ca and P elements, which emerged as corrosion products, suggested that the generated parts were suitable for bone implantation. Cell viability experiments conducted with MC3T3-E1 pre-osteoblast cells showed promising in vitro cytocompatibility	[26]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Mg-Zn-Zr	Understanding corrosion behaviour of Mg-based alloy manufactured with binder jet printing	General usage for biomedical purposes	The Mg-Zn-Zr powder, with particle sizes ranging from 60–70 μm, was utilized in inkjet printing to fabricate parts which were later sintered at different temperatures. Correspondingly, for reference purposes, control samples were produced by conventional casting techniques. The corrosion tests carried out at a temperature of 37 °C indicated that corrosion rates were significantly higher in parts sintered at lower temperatures. Porosity was a significant factor contributing to the non-uniformity of corrosion across the surface of the samples. It was determined that the binder jetting process, along with its microstructural variances, influenced the corrosion behavior of the materials. The comparison of corrosion rates among coatings of hydroxyapatite, polylactic acid, and epoxy on pores demonstrated that HA coatings were the least resistant	[23]

(continued)

Table 1 (continued)

Material	Aim	Application	Essential findings and details	Ref.
ß-TCP and bioactive glass	Investigating feasibility of 3D printing ß-TCP and biocompatible glass composites	Large scale bone implants	The ball milling technique was used to obtain the ß-TCP-BGH composite, followed by a spray-drying process at 230 °C to form granules. These composite granules were subsequently utilized in 3D printing, based on CT imaging data, to create implants. CAD software was employed to develop bending specimens, which were additively manufactured and sintered at a temperature of 1000 C. It was determined that the presence of glass did not influence the manufacturing process. The resulting components possessed a 4-point bending strength of 14.9 MPa	[27]

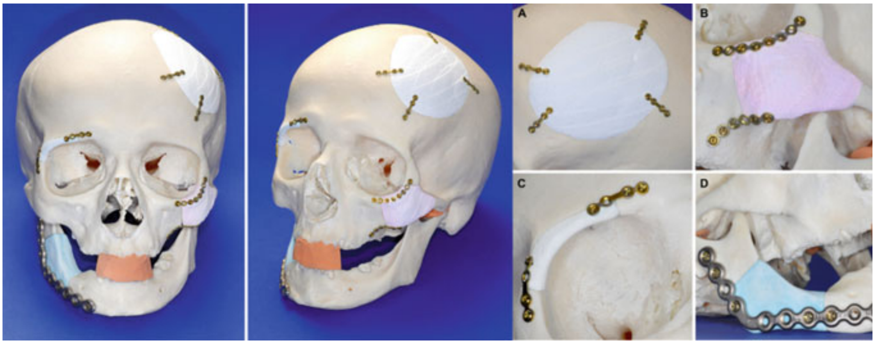

Fig. 4 Calcium phosphate implants produced for maxilofacial and cranium defects; **a** calvarium, **b** zygoma, **c** orbital rim, and **d** use in mandibular defects [19]

Researchers have been investigating the possibility of manufacturing bioinert and biodegradable metals through the binder jetting method. Sheydaeian et al. utilized a blend of 97% spherical titanium powder and 3% PVA powder to fabricate porous pure titanium implants with various layer thicknesses, intended for orthopedic bone implants. These implants, sintered at 1400 °C, exhibited porosity variations of up to 5% across different layer thicknesses. However, there was no significant change in mechanical characteristics [22]. Similarly, Kuah et al. utilized the binder jetting technique to create biodegradable porous Mg-Zn-Zr-based parts and studied their corrosion behavior in a PBS solution. The study found that the corrosion rate increased with increasing porosity and examined the effects of hydroxyapatite and polylactic acid coatings on the porous Mg-Zn-Zr parts. The results indicated that the PLA coating provided better corrosion protection. These findings demonstrate the potential of using binder jetting technology to produce bioinert and biodegradable metals for a range of medical applications [23].

3.2 Powder Bed Fusion for Biomedical Implants

The powder bed fusion method, which employs an electron beam or laser light to combine powders, is typically used. Various approaches are employed depending on the laser or electron beam strength, resulting in four powder bed fusion techniques. Selective laser sintering (SLS) and direct metal laser sintering (DMLS) utilize a powerful laser to join powders without melting, whereas selective laser melting (SLM) and electron beam melting (EBM) techniques selectively melt and weld powders [28]. The SLS production process involves three stages. First, the platform is lowered, then powder is spread, and, finally, laser joining is done using process parameters such as scan speed, laser power, spot size, and layer thickness. The process is repeated until the model is completed. The slicing program is used to set all of these parameters before printing. However, even if complete melting of powders is achieved in the production of thermoplastic materials, partial melting may occur during laser fusion. The selective laser sintering process differs from the sintering technique employed in powder metallurgy, with particles merging in mere seconds as compared to hours [29]. The process steps of the SLM method are very similar to the steps of the SLS method. The biggest difference in the SLM method is the selective joining of metal powders by melting. The range of metallic materials is fairly broad in the SLM technique, and materials can be produced with great sensitivity and a wide spectrum with this method.

Metallic glasses can be manufactured using the SLM process, along with alloys and composites based on Al, Ti, Fe, Ni, Co, and Cu. Unlike the SLS and EBM processes, the SLM method necessitates an inert environment. The EBM method is equivalent to the SLM method in terms of melting the particles to combine them. The powder bed's temperature is preserved at over 870 K in the EBM process, while laser beams are used to blend powders in the SLM and SLS procedures. Additionally, the printing process is significantly impacted by factors such as preheat temperature or platform temperature. The EBM method's use is restricted to Ti GR 2 and GR 5, Cobalt, and Inconel 718 powders due to the high powder bed temperature [30].

Powder bed fusion techniques are employed to produce implants for biomedical applications such as dental, load-bearing implants, bone tissue engineering, and cardiovascular stents. Bioinert applications primarily employ Ti and Co-based implants that are manufactured using the powder bed fusion technique, while biodegradable implant applications use Zn, Mg, and Fe-based implants. Ti-based implants, having an elastic modulus of around 110 GPa which is analogous to natural bone, have a lower stress shielding effect and are more extensively studied for load-bearing implants. They have high strength, low density, excellent corrosion resistance, and a high level of biocompatibility. Porous structures aid in lowering the elastic modulus of titanium implants, thus reducing the stress shielding effect and bone resorption, which can lead to implant failure [31]. Scaffolds made of Ti-6Al-4V powder with varying pore sizes and porosities for load-bearing bone implant applications were constructed by Zumofen et al. using the SLM method. The beam-based diamond, hexagonal, and cubic scaffolds were characterized using compression tests and a cell viability test. The cubic scaffold was the most similar to the cortical bone, with a high compressive strength of 151 MPa and stiffness of 4.9 GPa. Shape and pore size had no impact on Saos-2 cell proliferation [32].

Al and V-free Ti alloys have been examined for load-bearing implants as an alternative to Ti-6Al-4V alloy, which is the most commonly investigated Ti alloy for this purpose [33]. Ti-Ta alloys have been developed as a possible substitute for Ti-6Al-4V alloy. Song et al. produced Ti-50Ta bulk structure and found that it is mechanically superior to Ti-6Al-4V alloy, with a tensile strength of 924.64 ± 9.06 MPa and an elastic modulus of 75.77 ± 4.04 GPa [34]. Soro et al. created a porous scaffold for load-bearing implants from Ti-25Ta alloy. These scaffolds were produced in cylindrical form using Schwarz-P unit cells and had porosity ranges of 25–42–64%. They were found to be promising load-bearing implants, exhibiting high ductility and low modulus of elasticity, with an elastic modulus range of 14–36 GPa [35]. Additionally, Soro et al. produced scaffolds from Ti-25Ta alloy using Schwarz-P, Schwarz Diamond, and Gyroid unit cells and determined that these scaffolds had good cell viability in in vitro cell culture tests. These scaffolds showed an elastic modulus similar to cortical bone, with values of 15.8 GPa, 18.9 GPa, and 14.3 GPa for Gyroid, Diamond, and Schwarz-P scaffolds, respectively [36]. Therefore, Ti-Ta alloys, with their superior mechanical properties and low cytotoxicity, are a promising alternative to Ti-6Al-4V alloy for load-bearing bone implants.

Ackers et al. developed Ti-4.5Ta-4Fe-7.5Nb-6Zr (TTFNZ) alloy as an alternative to Ti-6Al-4V alloy for load-bearing implant applications. They investigated the impact of process parameters during powder production and additive manufacturing on heat treatment, shrinkage, compression, indentation, corrosion, and PVD coating characteristics. The findings of their tensile tests revealed that TTFNZ is mechanically superior to Ti-6Al-4V and Ti-Nb-Zr alloys, with a strength of 1271 MPa, making it a suitable candidate for biomedical load-bearing implants [37]. Zhou et al. studied the mechanical properties of Ti-6Al-4V alloy and the effect of adding 2% TiB by volume on those properties. The results showed a 25–36% improvement in both tensile and compressive strengths, along with a 14% increase in microhardness, which was attributed to Hall–Petch strengthening [38]. These findings demonstrate the potential for TTFNZ as an alternative to Ti-6Al-4V alloy for load-bearing implant applications while also highlighting the ability to enhance the mechanical properties of existing alloys through minor modifications.

Titanium-based implants are being researched as load carriers, as well as in the field of dentistry through powder bed fusion processes. Hou et al. produced porous scaffolds for dental implants through ball milling of Hydrogenation-dehydrogenation (HDH) Ti powder and selective laser melting. Porosity of 50–60% and 70% was achieved, with compression and permeability tests being carried out to evaluate the suitability of cylindrical specimens. Porous scaffolds formed from Schwarz-P unit cells, with 60% porosity, demonstrated ideal properties, yielding an elastic modulus of 9.7 GPa and a yield strength of 163.2 MPa. Permeability tests yielded a value range of $0.66–6.88 \times 10^{-9}$ m^2, which fell within the appropriate range compared to human bone ($0.01–12.10 \times 10^{-9}$ m^2). This research supports the potential application of these implants in dentistry [39]. Similarly, Xu et al. created implants using the gyroid unit cell with high compressive strength ranging from 206.1 to 477.5 MPa. The implants' pore ratios were the only variable. The scaffolds exhibited corrosion resistance with a corrosion rate of 2.5×10^{-4} mm/year and excellent biocompatibility, as demonstrated by the in vitro MC3T3-E1 cell culture experiments [40]. Selvaraj et al. developed a cranial implant for a 38-year-old patient using 3D imaging and selective laser melting, as shown in Fig. 5. They successfully implanted the cranial implant, made of the Ti-6Al-4V alloy, into the patient whose right temporosagital region of the skull was damaged in a car accident [41]. Lastly, Mcgee et al. created patient-specific cardiovascular stents using Ti-6Al-4V via selective laser melting. They used CT images of a 4-year-old child with congenital heart disease to fabricate the stents, which resulted in a deviation of 80 μm in the 500 μm designed beams. The surface roughness of the stents increased after etching, which could potentially enhance biocompatibility as per the research on the impact of etching on stents made using additive manufacturing [42].

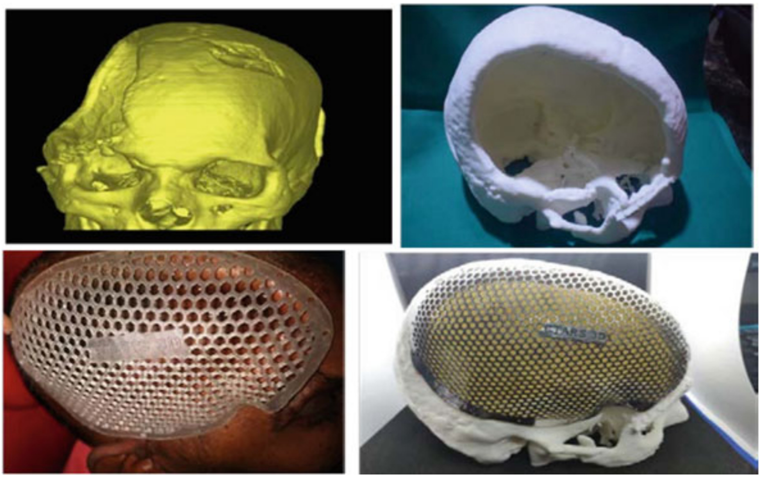

Fig. 5 Models for skull damage caused by traffic accidents and cranial implant produced by selective laser melting method [41]

In addition to titanium-based implants, 316L stainless steel implants, made by the powder bed fusion process, are utilized in many biomedical fields, including short-term implants, load-bearing implants, stents, cranial implants, dental implants and bone tissue scaffolds [43]. Čapek et al. produced bone scaffolds that had an approximately 90% porosity rate, and mechanical properties akin to sponge bone. Mechanical testing of scaffolds cut into rectangular shapes cultured with human osteosarcoma U-2 OS (ATCC HTB-96™) cells showed that porous scaffolds exhibited mechanical properties close to sponge bone, with an elastic modulus of 0.15 GPa and compressive yield strength of 3 MPa [44]. Selective laser melting was used by Jiang et al. to create face-centered cubic (FCC) meshes for rib implantation. They also observed differences in the chemical and physical structure of scaffolds printed at different laser energy densities. Moreover, FCC-based scaffolds produced at an energy density of 125 J/mm^3 were capable of being produced, exhibiting high strength and mechanical properties comparable to human rib bones [45]. Co-based alloys are another metal made through the powder bed fusion process, suitable for use in permanent implantation. Co-Cr based alloys exhibit high wear and corrosion resistance, with the Cr_2O_3 layer formed on their surface showing high resistance to corrosion [33]. Han et al. produced Co-Cr scaffolds tailored for load-bearing implants revealing the dependence of stress levels on the unit cell type and size. The determined elastic modulus and compressive strength of Co-Cr scaffolds ranged from 7.18–16.57 GPa and 271.53–1279.52 MPa, respectively [46]. Hedberg et al. conducted a study employing selective laser melting to examine the fabricability, microstructure, and metal release characteristics of Co-Cr-Mo-based dental alloys in biological fluids. In addition, the identical alloy was also produced using traditional casting to ensure comparison. Due to quick cooling, the highly fine-grain structure and higher Mo ratio at the cell boundaries were both observed. Moreover, the martensitic ε phase increased at the surface in comparison to its cast counterpart, leading to a higher susceptibility to corrosion [47]. Furthermore, Wei et al. investigated how post-processing heat treatment would impact the fatigue strength of orthopedic implants made of Co-Cr-Mo alloy by utilizing the electron beam melting method. By using heat treatment to alter the phases in the microstructure, fatigue strength was improved [48]. Additionally, powder bed fusion has recently been used to make and test tantalum (Ta) based implants intended for use in bio-inert implant applications. Chen et al. produced Ta-based gyroid unit cell implants to meet the requirements of load-bearing orthopedic applications. Although the Ta implants were entirely dense and made without fractures, their grain size was higher compared to their forged equivalent. Moreover, Ta resulting from additive manufacturing exhibited greater cell adherence and proliferation in comparison to forging, demonstrating the high precision fabrication of porous tantalum scaffolds [49].

Powder bed fusion techniques enable the production of not only bioinert implants but also biodegradable metals and their alloys for various implant applications. Biodegradable metals, such as magnesium, iron, and zinc alloys, are widely utilized. Among the biodegradable metals, Fe-based implants have the highest strength [50]. Due to their excellent mechanical properties, favorable corrosion behavior, and magnetic properties as a result of their austenitic phase, many researchers have investigated Fe-Mn alloys [51–54]. Again, Si and Ag elements were alloyed with Fe and tested for various biomedical applications [55, 56]. For load bearing applications, Manshadi et al. developed scaffolds from the Schwarz P unit cell with 60% porosity. The scaffolds produced by mixing the gas atomized Fe-35Mn powder with 1% silver powder had a total porosity of around 52%. In Archimedes tests, the internal porosity rate varied between 0.63 and 1.35%. The iron-based biodegradable scaffold's degradation rate was also accelerated by the addition of 1% Ag, but the elasticity modulus remained unchanged and the compressive strength increased [57]. In contrast to Fe-Mn-based biodegradable iron alloys, Gao et al. used gallium for the first time. Fe-19 Ga alloy powder was produced by gas atomization, and a cylindrical form was produced via selective laser melting. The examination conducted after the manufacture revealed uniform alloying and grains in the direction of production. Additionally, culture experiments using MG-63 cells showed satisfactory viability, and a corrosion rate of 0.09 mm/year was observed [58].

Magnesium has a significant place among biodegradable implants due to its high strength-to-density ratio. However, magnesium exhibits relatively poor corrosion resistance when alloyed with elements like Fe, Ni, Co, and Cu. This makes it particularly vulnerable to corrosion caused by micro-galvanic effects [59]. As a result, high susceptibility to corrosion and toxic effects caused by excessive hydrogen accumulation can negatively impact the mechanical characteristics and biocompatibility of magnesium implants. To preserve the necessary mechanical properties for a certain period of time by degradation of magnesium at an appropriate rate, several researchers have started investigating ways to improve its corrosion resistance [60]. For instance, Lovaiová et al. produced a cubic sample with an 8 mm edge using gas atomized

WE43 powder and studied the mechanical, corrosion, chemical, and biological characteristics of Mg-based parts. Although the parts had relatively small grain size, the immersion test revealed that the corrosion rate was 2.6 mm/year, which was too quick [61]. To overcome this issue, Xie et al. constructed orthopedic implant scaffolds from Mg-Nd-Zn-Zr alloy, which demonstrated good osteoinductivity in cell viability experiments using MC3T3-E1 cells [62].

Zinc does not corrode as slowly as iron, nor as fast as magnesium. Furthermore, zinc, one of the essential elements found in the human body, has no hazardous impact on the human body if properly degrades. However, manufacturing zinc-based implants using the powder bed fusion method is challenging due to the low mechanical properties of such implants compared to magnesium and iron-based implants [63]. Additionally, the melting and boiling points of zinc are 419.5 °C and 907 °C, respectively, and easily volatile zinc powders can lead to reduced manufacturing quality. As a result, process optimization is essential. To overcome these challenges, Wang et al. employed selective laser melting to generate 8 mm-sided cubic components for biomedical orthopedic implants. The mechanical properties of these components were found to be superior to those produced by casting [64]. Table 2 provides a summary of some bioinert and biodegradable biomedical implant studies and critical findings obtained via the powder bed fusion method in the literature.

3.3 *Vat Photopolymerization Method for Biomedical Implants*

In the literature, the vat polymerization process is often referred to as stereolithography (SLA). Yet, depending on the kind of light source employed, it is sometimes called digital light processing (DLP). In this technique, liquid polymers are solidified selectively with the aid of a light source. SLA/DLP technique is one of the most precisive additive manufacturing technique with the highest accuracy, the best surface finish and the least material loss. Although it is basically based on the solidification of photopolymer resins, it makes it possible to produce ceramic and metallic materials with high accuracy using powder doped slurries [69]. In particular, ceramic powder-added slurry has been the subject of much SLA and DLP research in recent years. Porous or dense structures may be printed with almost perfect precision. Tricalciumphospate (TCP), hydroxyapatite (HA), and calciumphospate (CaP) are the examples of examined potential biomedical ceramic implants [70]. SLA method was used by Zhou et al. to produce spine model using TCP bioceramic slurry for hard tissue applications. For model construction, 40–48 wt% powder was employed. Slurry with a layer thickness of 20 microns was successfully created by adding 1% SiO_2 as sintering agent and 2% silane KH-560 as dispersant. Then the slurry was milled for 15 h at 220 rpm with high-energy milling. After sintering, the manufactured implants had a density of 85.8% [71]. Zirconium dioxide (ZrO_2) ceramic teeth were manufactured by Chen et al. using the DLP process. The optimum solid powder ratio for teeth sintered at 1500 °C was found to be 42%. Moreover, ceramics were created with great precision using a 3-s exposure time. As compared to dry

Table 2 Applications of biomedical implants produced by the powder bed fusion method

Material	Aim	Application	Essential findings and details	Ref.
Fe-Mg	Manufacturing scaffolds by additive manufacturing from a supersaturated Fe-Mg solid solution by mechanical alloying	Orthoapedic bone implants	In this study, the Fe-Mg solid solution powder used for selective laser melting was produced using a high-energy ball mill instead of the gas atomization method typically found in the literature. The powders were milled for 40 h at 300 rpm and were then utilized to fabricate cylindrical porous scaffolds using laser parameters of 100 W and 100 mm/s for beam sizes of 500 µm and pore sizes of 800 µm. The quick melting and cooling afforded by the powder bed fusion method enabled the efficient production of the required composition's supersaturated solid solution powders. The Mg solubility was reduced from 8.5 to 7.8% during additive manufacturing. The supersaturated solid solution and high Mg content facilitated the intended outcome by accelerating the decomposition rate while exhibiting high biocompatibility and supporting cell growth	[65]

(continued)

Table 2 (continued)

Material	Aim	Application	Essential findings and details	Ref.
AZ61-Ce	Improving the mechanical and corrosive properties of AZ61 alloy by addition of Cerium (Ce)	Bone implants	Gas atomized AZ61 powder was used to produce pieces using the selective laser melting method. The powder was then mixed with varying amounts of Ce element using ball milling for 4 h at 200 rpm. Addition of 1.2% Ce increased the compressive strength value from 145.93 to 225.61 MPa. Also, by reducing the corrosion current density from 159.36 to 12.5 A/cm^2 for the 1.2% Ce ratio, the corrosion resistance was significantly increased. This improvement in resistance is believed to be due to the replacement of Mg17Al12 phase by the Al4Ce phase in the AZ61 alloy. However, adding more than 1.2% Ce led to the coarsening of the Al4Ce phase, which ultimately resulted in decreased strength of the alloy. The structure of the developed alloy was found to be suitable for use in biodegradable bone implants, facilitating cell growth and reducing corrosion rate	[66]

(continued)

Table 2 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Zn-Ce	To improve antibacterial and mechanical properties of orthopedic zinc implants with the addition of Cerium	Bone implants	Pure zinc powder produced via nitrogen atomization was combined with 1–3% Ce using the ball milling method at 200 rpm. The samples were then printed using a laser spot diameter of 70 μm, a scanning speed of 300 mm/s, and a laser power of 50 W. The addition of 2% Ce led to a significant increase in the tensile strength of the pure zinc from 103.6 to 247.4 MPa. Creep behavior was also comparable to the tensile test results. The inclusion of Ce is thought to enhance the corrosion resistance of the material by facilitating the formation of a passive oxide film on the surface. Additionally, the addition of Ce resulted in improved antibacterial properties, with the inhibition zone test reflecting an increase in the antibacterial rate from 34.28 to 81.36% when tested with Escherichia coli bacteria. Overall, the addition of Ce to the Zn-based powder resulted in enhanced mechanical and biocompatibility properties	[67]

(continued)

Table 2 (continued)

Material	Aim	Application	Essential findings and details	Ref.
Cp-Ti	To examine the effects of design parameters on production, mechanical and permeability properties with additive manufacturing	Dental implants	Dental scaffolds produced through selective laser melting were designed and produced utilizing gyroid-based unit cells with varying porosity values. To create porosities ranging from 20 to 60%, pore sizes of 303.7 to 635.3 μm were employed. The 30% porosity scaffolds exhibited an elastic modulus of 14.6 GPa and a compressive yield strength of 351.5 MPa, making them mechanically compatible with human bone. Implants with 20–40% porosity values were found to be ideal, with a corrosion rate of $3.7–22.7 \times 10^{-3}$ mm/year and an MC3T3-E1 cell toxicity level of 0–1	[40]
Nitinol	Investigation of the effects of powder bed fusion production parameters and heat treatment effects on microstructure and mechanical properties for nitinol stents	Peripheral or cardiovacular stent implants	Powder bed fusion was used to implement 3D-printing employing plasma atomized spherical NiTi powders, with a fixed 20 μm layer thickness, laser power ranging from 60 to 100 W, and scanning speeds between 115 and 250 mm/s. The nanoindentation method was utilized for determining the elastic modulus and hardness of the stents. The strut thickness of the stents increased as the laser energy density increased, despite being nearly fully dense. Successful manufacturing of both zigzag and Palmaz-Schatz designs have been shown. Energy densities of 0.3–0.8 J/mm demonstrated more effective manufacturing of the Zigzag stent geometry as compared to the Palmaz-Schatz model. The rate of nickel evaporation increased with rising laser intensity. The fabricated stents exhibited an elastic modulus similar to that of a traditional manufacturing process	[68]

pressing, ZrO_2 ceramics with 12.62 GPa hardness and 6.11 MPa $m^{1/2}$ fracture toughness showed improved mechanical properties. In addition, studies with mesenchymal cells showed that ceramics with high biocompatibility have a strong potential for personal oral applications [72]. Production with metallic inks is not yet available in the literature for biomedical implants. Studies are very limited since the high density of metallic particles may cause undesirable conditions such as sedimentation.

3.4 Material Extrusion Methods for Biomedical Implants

Fusion deposition modeling (FDM) is the most popular technique for material extrusion, which directly produces thermoplastic polymers from filaments. A thermoplastic polymer filament is melted at an appropriate temperature using an extruder, forming it into layers. Compared to metals and ceramics, these filaments have a much lower melting temperature. Although FDM printers, which range in price from $300 to $100.000, are less sensitive and have lower surface quality than the vat polymerization method, they can produce polymers with greater accuracy of ±127 μm and a variety of biomedical grades. This approach is suitable for biomedical implant polymers like polycaprolactone (PCL), polyetheretherketone (PEEK), polylactic acid (PLA), and medical-grade acrylonitrile-butadiene-styrene (ABS) [24]. Oladapo et al. produced pure and PEEK calcium hydroxyapatite (cHAp) composite filaments for orthopedic bone implant applications using FDM and medical PEEK-based pellets. Moreover, the craniofacial implant was created according to the tomography file's image without any issues. Load-bearing implants with high biocompatibility exhibited appropriate mechanical characteristics [73]. Yang et al. developed drug delivery implants utilizing the FDM method from Ibuprofen (IBP)-chitosan (CS)-PCL composite filaments they produced using a twin-screw extruder. Altering the CS and drug ratio accomplished controlled drug release. The tensile strength of the produced implants decreased as the CS-IBP ratio increased. The implant with high biocompatibility can be utilized in face plastic surgery or tissue repair, according to the researchers [74].

In recent years, the FDM process has been explored for the fabrication of biomedical implants from metallic, ceramic, and composite materials, rather than just polymer-based implants. A polymer binder may be used to create metallic and ceramic filaments. The principle of production shown in the manufacture of thermoplastics remains unaltered for the FDM process. This technique finds suitable utility in the fabrication of a bevy of metallic alloys including but not limited to stainless steel, titanium, aluminum, copper, and nickel. However, ceramic and metallic components are required to undergo debinding and sintering processes after printing [75]. Zhang et al. utilized FDM and selective laser melting to print Ti-6Al-4V. Microstructures, phase changes, hardness, porosity, and residual stress ratios were investigated. The SLM method had the smallest porosity rate at 3.6%, whereas the porosity ratio of the Ti-6Al-4V alloy made by the FDM method decreased from 24.99 to 10.96% as the sintering temperature increased from 900 to 1340 °C [76]. Nötzel et al. developed

Al_2O_3-Paraffin-LDPE composite filaments utilizing a single screw extruder system. Disc-shaped pieces were successfully produced using sintered filaments comprised of ceramic particles from 10 to 60% by volume [77].

Material extrusion techniques can use ceramic and metallic pastes or suspensions, as well as filaments, to create products. A syringe or plunger serves as the driving mechanism in this extrusion system, and a heater can be used to adjust the viscosity or melt plastic binders. After the green part is produced, a debinding process is applied to the paste or suspension, which is layered on a bed like FDM. Subsequently, the final product is sintered at a specific temperature with a slow heating rate, taking into account the possible occurrence of shrinkage after debinding and sintering [76]. Dairaghi et al. utilized an extrusion system to create middle ear bones from a ceramic paste. Calcium Phosphate-Hydroxyapatite composite paste, known as Osteoink, was used to produce the models [78]. Similarly, Slámečka et al. used a material extrusion method to produce biomedical implants, using gas atomized grade 1 Titanium powder and 10% by weight bovine gelatin solution to create scaffolds. Sintering affects the porosity of the scaffolds, which directly correlates with compressive fatigue strength. Even after 106 cycles of testing, the mechanical properties of the scaffolds remained stable. Their normalized fatigue strength was 62% of their yield strength, demonstrating that their mechanical properties were nearly as good as those produced by powder bed fusion [79]. Table 3 provides further examples of biomedical implant studies conducted using the material extrusion method.

4 Conclusion

Recent years have witnessed a significant surge in patient-specific applications, particularly in the scope of orthopedic and dental implants, tissue engineering, and craniomaxillofacial treatments with additive manufacturing. The provision of personalized 3D-printed drugs and the ability to fabricate complex designs are among the salient features of additive manufacturing, offering numerous advantages to produce new generation materials of the utmost quality. Additive manufacturing will occupy an even more prominent position in the biomedical materials market, which is witnessing extraordinary growth. As we have demonstrated in this book section, additive manufacturing techniques offer the opportunity to fabricate biomedical implants with high precision and desired shape specific to their applications and their deployment site.

Table 3 Biomedical implant studies produced by the material extrusion method

Material	Aim	Application	Essential findings and details	Ref.
Ti-6Al-4V	Manufacturing patient specific implant properly	Maxillofacial implant	1.75 mm diameter filament was produced from a metal-polymer mixture with 59% metal powder by volume. A maxillofacial implant was designed using Cone Beam Computed Tomography (CBCT) to enable the attachment of a dental implant in an 85-year-old female patient. The design was successfully manufactured using metal fused filament fabrication, with ideal support structures built for the first time. The implant's center had a relative density ratio of 81%, with 6% closed porosity and 13% open interconnected porosity. The method yielded a hardness of 6.5 HRC, which is lower than the typical hardness values obtained with Electron Beam Melting (EBM) and Selective Laser Melting (SLM) methods, which are around 45 HRC. Thus, this study highlights the efficacy of using a metal-polymer mixture and fused filament fabrication for creating intricate implants	[80]

(continued)

Table 3 (continued)

Material	Aim	Application	Essential findings and details	Ref.
PLA-Mg	To investigate the fabricability of PLA-Mg composites with a low-cost 3D printer	Anterior cruciate ligament screws	To prepare composite filaments, 500 µm Mg powder was milled using a planetary ball mill and a cryogenic mill for 48 h. Subsequently, filaments were produced using a single screw extruder that contained 100 and 125 µm 6 g Mg powder and 150 g PLA powder. In all compositions, 2 g of liquid vitamin E was applied. The filaments, with a diameter of 1.75 mm, were successfully produced using a single screw extruder, following which the anterior cruciate ligament screws were fabricated	[81]
Fe-Mn	Investigation of the effect of different Mn ratios by preparing a metallic ink	Bone implants	Pure iron powder was combined with Mn powder at concentrations of 0%, 10%, 30%, 50%, and 70%. Two different binders were used, either 2 g PLA or 8 g dichloromethane polymer solution. Scaffold structures with porosities of 10–50% and 70% were produced, each measuring 6 × 6 × 12 mm. Alongside these structures, a femoral bone was created using an extrusion pressure of 0.3–0.6 MPa, a layer thickness of 220 µm, and a writing speed of 10 mm/s. Scaffolds with 10–70% porosity values had a modulus of elasticity that ranged from 0.03 to 4.27 GPa. Scaffolds that exhibited properties similar to those of natural bone indicated promising potential for Fe bone implants	[82]

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Chapter 12
Applications of Additive Manufacturing in Construction and Building Industries

B. Mallikarjuna, M. N. S. Hareeswar, and P. C. Sharath

Abstract The construction and building sectors are labor intensive, have a shortage of skilled people, and face low productivity. The automation and digitalization of all relevant steps in construction and building may appear to resolve the issues. Additive manufacturing (AM), also known as three-dimensional (3D) printing, uses computer-aided design data to build complex physical objects by adding material layer-by-layer without using dies, tools, jigs, and fixtures. AM is used in various sectors, including aerospace, biomedical, space, automotive, and others. More recently, AM has gained popularity in construction and building due to its tremendous benefits, such as design freedom, material saving, mass customization, fast prototype, and functional parts. In the construction industry, extrusion-based additive manufacturing processes, commonly known as 3D concrete printing (3DCP) are used. This chapter describes the 3DCP process, process parameters, materials and focuses on the construction applications. The challenges and prospects of 3DCP in construction and building fields are highlighted.

Keywords Digital construction · Extrusion-based 3D concrete printing · Concrete · Construction and building

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1 Introduction

Global population is expected to reach 8.9 billion by 2050. Annually the demand for construction materials persists to increase by more than 23 trillion kg of concrete. The construction and building sectors contribute around 30% of global greenhouse gas emissions annually [1]. This is directly/indirectly contributing to global warming and climate change. Construction and building sectors are labor intensive for potentially dangerous tasks [2, 3]. Hence the effective use of resources of construction materials is optional. Researchers are working on finding new construction routes. Towards this end, additive manufacturing (AM) technology has been developing since the 1980s [4, 5]. It was the result of the development of technologies such as computer-aided drafting (CAD), computer-aided manufacturing (CAM), robotics and control systems [5, 6]. It was initially proposed for the fabrication of aesthetic prototypes and therefore came to be known as Rapid Prototyping (RP). Geographically, technology was called different names, such as layer manufacturing, digital fabrication, desktop manufacturing, and freeform fabrication [5, 7]. In 2009, the ASTM F42 Committee was standardized, and all the names fall under additive manufacturing [7, 8]. Additive manufacturing is commonly called 3D printing. AM processes start with a computer-aided design (CAD) file and then convert it to a standard triangulation language (STL) file. In this process, the CAD drawing surface is represented with triangles. Then STL file is sliced into tool path, containing the information for each layer to be printed [5, 9]. The initial use of materials was primarily polymer, liquid, and filament forms. Later, it expanded to several materials, including metals, ceramics, composites, biopolymers, etc., [6, 10–12] for aerospace, automobiles, marine, military, and healthcare [13, 14]. There are seven families of additive manufacturing according to ASTM/ISO standards such as Vat photo-polymerization, material extrusion, powder bed fusion, sheet lamination, material jetting, binder jetting, and directed energy deposition [15]. Each machine is capable of processing specific materials [6, 16].

Cement-based additive manufacturing processes are often called 3D concrete printing (3DCP) [19]. The 3DCP comes under the material extrusion-based additive manufacturing process because of concrete extrusion through the nozzle, alike fused deposition modeling (polymer and composite materials filaments) [3, 20, 21]. Binder jetting additive manufacturing is also used for 3DCP of small-size components in the construction industry (powder and binder as feedstock materials) [22]. Several researchers have reported the fabrication of various construction and building applications such as concrete arches and vaults, concrete formwork, rain collection tank, and formwork for stairs and buildings [23–28]. Since its inception in 1997, this technology has been rising swiftly in large-scale construction [24, 26, 28–30]. Buswell et al. [17] 2018 reported that the 3DCP in construction and building growth is exponential, as shown in Fig. 1a. The number of projects that have been completed by academia and industries has increased. The cumulative projects increased by 60% between 2012 and 2018 [17]. The global market research trend shows that the 3DCP market growth rate is 14.05% between 2017 and 2019 Fig. 1b. The actual market is even more significant, expected with technological advancement, the way of understanding the processes, materials, and digital planning and building information modeling (BIM). Therefore, the aspects like extrudability, printability, and buildability are studied to print various materials such as concrete, geo polymer, and clays [3, 31, 32]. Using 3DCP in construction and building has many advantages: time, cost, geometric freedom, sustainability, and safety. 3D Printing can reduce the construction time considerably as compared to conventional construction methods. Cost reduction can also be a huge advantage. Ibrahim et al. 2022 [27] the construction time of an office in Dubai was 60% lower when compared to buildings of the same size built conventionally. Geometric freedom is also a considerable advantage when compared to conventional methods. The conventional methods were limited to generic shapes, but with the help of 3D printing, it is possible to achieve the architect's visual spectacle. Using 3D printing for construction can also be sustainable for the environment. It reduces the formwork involved in conventional methods and minimizes the waste of materials. Wu et al. 2016 [33] 3D printing eliminates unnecessary waste, reducing the impact on the environment and construction process by reducing the formwork needed, less wood is used, and saving trees from being cut down. 3D printing can also increase workplace safety and reduce injuries and fatalities, since it reduces hazardous work.

This chapter's motto is to shed light on the potential 3D concrete printing (3DCP) processes in construction and building applications. Mainly focused on the material extrusion-based 3DCP basics and its principle of deposition, concrete materials (mortar) and new future materials for construction applications, process parameters and their importance in 3DCP, applications of 3DCP in construction and building industries.

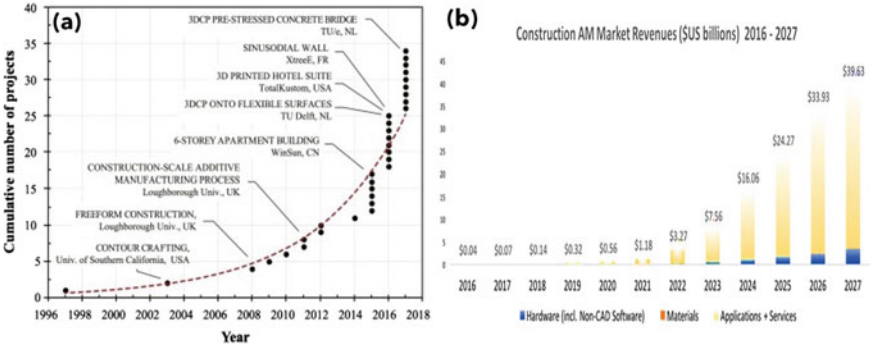


Fig. 1 **a** 3DCP projects growth in construction and building [17] and **b** Forecast of construction AM market revenue [18]

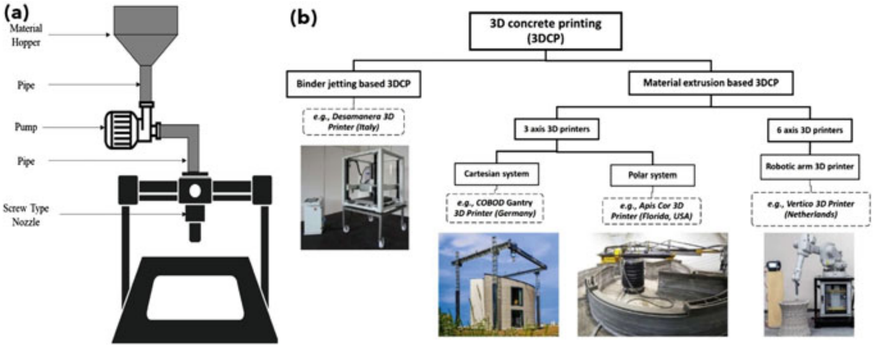


Fig. 2 **a** Illustration of various segments of the material extrusion system of a 3DCP (Reproduced from [34]) and **b** types of 3DCP

2 Material Extrusion-Based 3D Concrete Printing

The illustration of the material extrusion-based 3D concrete printing process is shown in Fig. 2a. The 3DCP comprises several segments, such as a hopper, pipes, pump, nozzle, and gantry. The concrete is poured into the hopper and pumped via a pipe to the nozzle. The large diameter nozzle extrudes material in the required amount [34]. The material is deposited on the substrate followed by the previous layer from a nozzle as G-code is generated layer-by-layer until the building or component is finished. Followed by post-curing and finishing processes. The 3DCP is classified into two types, as shown in Fig. 2b. The first type of 3DCP is binder jetting additive manufacturing, in which the powder and binder are used as feedstock material. The powder is fed to the table by a roller, and via a nozzle, a binder is applied selectively to build the layer. The second type of 3DCP can be classified based on the coordinate system (Cartesian, polar, robotic arm) [35, 36]. The first 3DCP was reported by the University of Loughborough for the feasibility of concrete printing and assessed the mechanical properties [37, 38]. The next by the Eindhoven University of Technology further explored the possibilities of 3DCP [39].

3 Gantry and Material Extrusion System

The gantry is a multi-axis (x, y, z) overhead bridge structure used in 3DCP [39]. Chandra et al. [3] analyzed various monolithic 3D printer gantry systems. It was observed that with the ability to produce versatile prints, superior dimensional accuracy, and fast printing speed, the 3-axis or 4-axis Cartesian gantries are better than the polar or robotic arm gantry systems for 3D printing. Betina et al. [35] analyzed the two types of gantries, Core-XY and the Delta, as depicted in Fig. 3a. The Core-XY is a sub-type among the 3-axis gantries. In the Core-XY gantry, the deposition nozzle, i.e., the printhead, moves on the X and Y axes while the build platform moves from top to bottom on the z-axis. Whereas the Delta gantry, the build platform is fixed, and the printhead moves spatially in a tetrahedral volume. It was found that the Core-XY gantry-produced parts have better dimensional accuracy and print quality than the Delta gantry. Kopets et al. [41] Conducted a vibrations analysis on a Core-XY gantry using the finite element analysis software. The simulation analysis was verified by having their printhead move with speeds ranging from 50 to 150 mm/s, which shall cause vibrations in the gantry ranging from 50 to 500 Hz. The selection of the gantry size is based on the building and architecture [37]. Similarly, several researchers have reported on the design and development of the gantry [39, 43].

The gantry carries the printhead/extrusion head. Generally, extrusion systems can be classified into three types, as shown in Fig. 3b. Netto et al. 2021 [40] reviewed the application of screw-based extrusion on various materials. Concepts of screw-based extrusion systems and their combinations are illustrated. The analysis emphasizes that the screw extrusion system at the nozzle gives more precise control. Archimedes Screw, auger drill bit, and pressure profile screw are the various readily available options for screw-based extrusion, as shown in Fig. 3c, d and e. Auger drill bit provides the maximum amount of volume flow through it. The issues such as clogging in the screw, inconsistent layer bonding, and improper filling were faced when using the other two mechanisms. Sean et al. 2017 [44] developed a screw-based extrusion system for a printhead to deposit polymer material that feeds in the form of pellets. Leng et al. 2020 [45] developed a conical screw for a nozzle which was utilized to extrude polymer material which was fed in the form of pellets. However, the inlet feed for the nozzle must be designed. Either a screw-based system or a plunger feed could be utilized for this purpose. Chaari et al. [46] have experimentally validated the use of a plunger feed system for the screw-based extrusion nozzle as the extrusion mechanism shown Fig. 4. The extrusion mechanism was based on Archimedes screw. This screw was incorporated into a Delta gantry and the aspects such as layer adhesion in print along with the extrudability of clay and materials alike were tested.

Jackson et al. 2019 [48] designed and developed a print head for asphalt deposition. Archimedes' screw mechanism was utilized for the extrusion at the nozzle. This mechanism was 3D printed using ABS polymer filament. It was experimentally verified that the 3D printed screw mechanism could be effectively utilized for extrusion at the nozzle for the pastes. Zeleny et al. 2017 [42] developed a plunger-based extrusion system, which was 3D printed, tested, and validated during experimentation. It was validated that the 3D printed gear mechanisms can be utilized for plunger systems as the replacement for the expensive NVRM gear mechanism. Li et al. 2015 [47] investigated the effect of a nozzle cap and its influence on the quality of layer deposition. It was observed that the nozzle cap enabled the printing of flat-layer beads and resulted in better layer adhesion (refer to Fig. 4b). Also, the improved adhesion between layers improves the print quality and mechanical properties. Rane et al. 2018 [43] systematically reviewed the various extrusion systems which were employed for the ceramic pastes. The work provides mathematical equations related to the nozzle diameter to nozzle moving speed, that is:

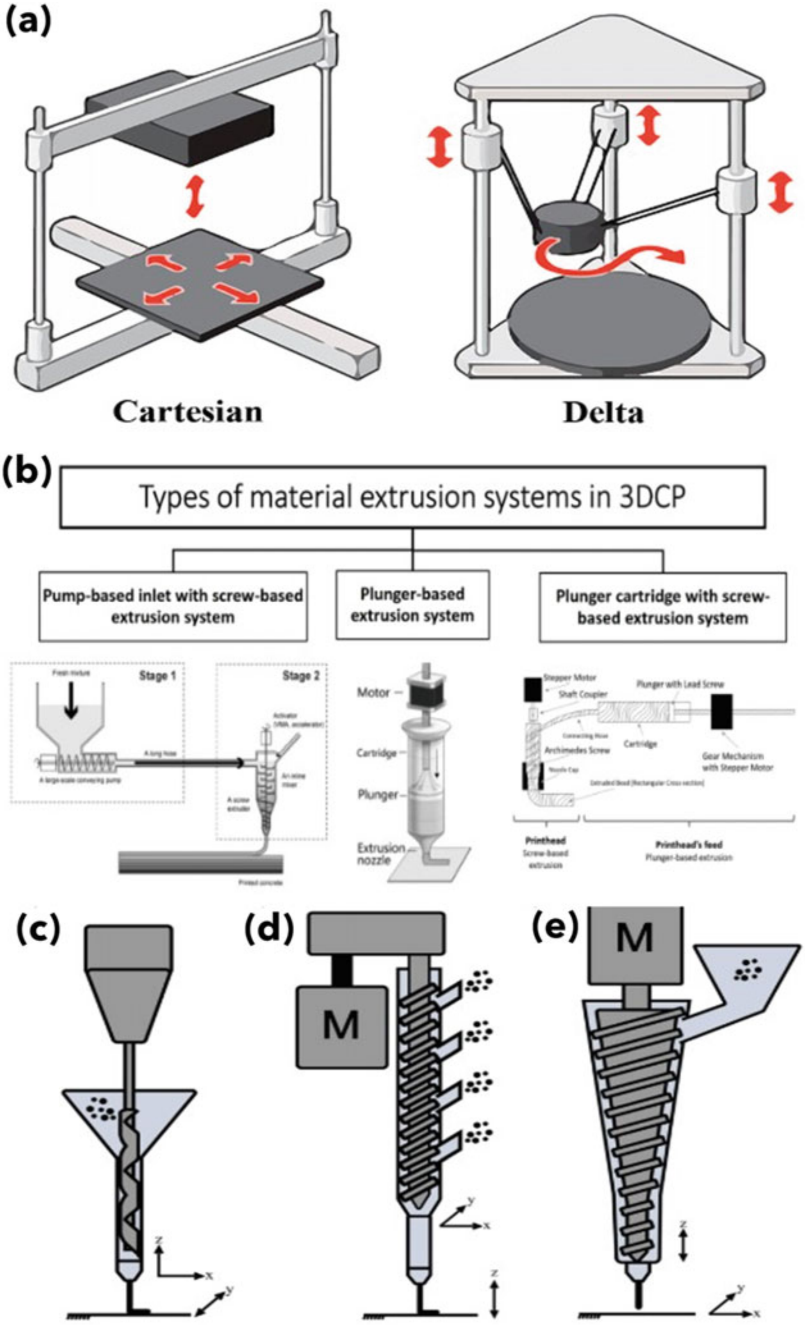


Fig. 3 **a** Schematic of Cartesian and delta printers (Reproduced from [35]). **b** Classification of the existing material extrusion systems in 3D concrete printers (Reproduced from [40]) and types of screw-based extrusion mechanisms. **c** Auger drill bit. **d** Multi inlet screw extruder. **e** Conical screw extruder (Reproduced from [40])

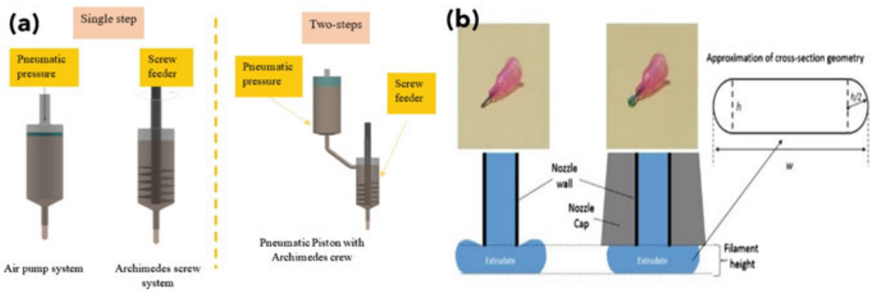


Fig. 4 **a** Illustration of plunger input for the screw-based extrusion nozzle (Reproduced from [46]) and **b** nozzle without a nozzle cap or its equivalent (left) and with a nozzle cap (right) (Reproduced from [47])

$$V_n \times h_c = D_n \times V_d \tag{1}$$

where V_n is the velocity of the nozzle, h_c is the critical layer height, D_n is the diameter of the nozzle, and V_d is the rate of extrusion from the nozzle. For a higher extrusion rate, a larger diameter of the nozzle can be adapted because these two parameters are directly proportional.

4 Materials

Concrete is a commonly used material in the construction and building industry [49]. Concrete can be obtained by mixing cement, sand, water, and aggregate in the right proportion. For example, the mixing of cement, sand, and water is called mortar. Therefore, material with the right properties is required in 3DCP, so that proper extrudability, printability, and hardenability can be achieved [50, 51]. The various concrete/mortar materials used in 3D printing, such as calcined clay cement, geopolymer, Portland cement, cement, silica fume, superplasticizer, and Calcium aluminate cement with ordinary Portland cement, [38, 52, 53]. Yuan et al. 2021 [54] developed a modified limestone calcined clay cement (LC3) composite for 3D printing by introducing silica fume (SF) and particle packing theory. Results show that when composites contain 33.33 Wt% calcined clay, 16.67 Wt% limestone powder, and 5 Wt% SF with a sand to binder ratio (S/B ratio) of 2.5. The dynamic yield stress, static yield stress, and structural recovery are significantly improved. The proposed mortar was extruded continuously with minimum defects and exhibited excellent shape retention during the printing process. Marczyk et al. 2021 [55] conducted a study on the development of hybrid materials based on a geopolymer or regular cement matrix for 3D printing. The raw materials were mixed with commercial quartz sand with a chemical composition: of 90.0–90.3% SiO_2, max. 0.2% Fe_2O_3, 0.08–0.1% TiO_2, 0.4–0.7% Al_2O_3, 0.17% CaO, 0.01% MgO. Chen et al. 2021 [56] investigated the effects on the flowability and buildability of blended Portland cement with calcined clay (CC) and limestone (LF). The percent of LF and CC can lower the flowability but increase viscosity modifying admixtures percentage (VMA%), which improves water retention capacity and shape retention property. Revelo et al. 2019 [57] Kaolinite clay-based ceramics and several low-cost ceramic powders, including talc, fly ash, and lime, have been tried in the extrusion additive manufacturing process. The water-to-clay ratios (W/C) used to create the samples ranged from 0.68 to 0.72. In terms of the clay contents, the additions were evaluated at 3.0, 5.0, and 7.0 Wt%. The samples with a 0.70 W/C ratio and fly ash addition, resulted in good workability, mechanical properties, and surface finishing. Long et al. 2021 [54] in this study produced a modified limestone calcined clay cement (LC3) composite with raw materials such as calcined clay, sand, silica fume, limestone, and cement. The dynamic yield stress, static yield stress, and structural recovery of composites may be greatly enhanced (containing 33.33 Wt% calcined clay, 16.67 Wt% limestone powder, and 5 Wt% SF with an S/B ratio of 2.5). Mortar flowability slightly decreased with the addition of supplementary cementitious materials (SCMs) such as calcined clay, limestone powder, and silica fume. However, the compressive strength continued to increase with an increase in the S/B ratio up to 2.5%. Panda et al. 2019 [21] This study looked into adding nano-attapulgite clay (NC) to high-volume fly ash (HVFA) and its effects on hardened and microstructural properties. As a result, utilizing NC improved the material's flocculation strength, which in turn led to greater yield stress without significantly affecting viscosity. The improved buildability and less distortion of the prepared mixes throughout the 3D printing process were noticed. Wi et al., 2020 [58] conducted the study on characterizing cement mixtures for concrete 3D printing. A mixture of cement, silica fume and superplasticizer were used with the Wt% of each of the constitute being as follows 97.5%, 2.5%, 1.5% respectively. Various samples were made with different Wt% and the mechanical properties of each sample was tested. It was observed that the silica fumes and superplasticizer improvised the yield stress and maintained the desired viscosity of the concrete mixture. Shakor et al. 2017 [22] analyzed the two specific cement mixtures, the first mixed in the print head and the second manually mixed. The cement mixture consists of calcium aluminate cement is 32.2% with 67.8% ordinary Portland cement. The porosity was low and compression strength was better for the manual mixture. The porosity level of composition without lithium carbonate is 62.292% (S170-C340), and with lithium carbonate at the same saturation level, the compressive strength increased. Tregger et al. 2010 [59] examined the rheological impact of clay mixtures on the microstructure of cement pastes. A cement control mix (CM), a cement-fly ash mix (FA), and a cement-high-range water-reducing mix (HW) were evaluated. Experiments on cement paste and concrete with the same matrix that measure shear and compressive rheology as well as green strength. It was found that the pure magnesium aluminium silicate clay, known as nano clay, was the most successful in enhancing stability. Similarly many researchers reported on concrete materials in the literature for the 3DCP [52, 60–63]. Also, sustainable materials development is under consideration for the 3DCP [50]. The following section discusses the influence of process parameters while building.

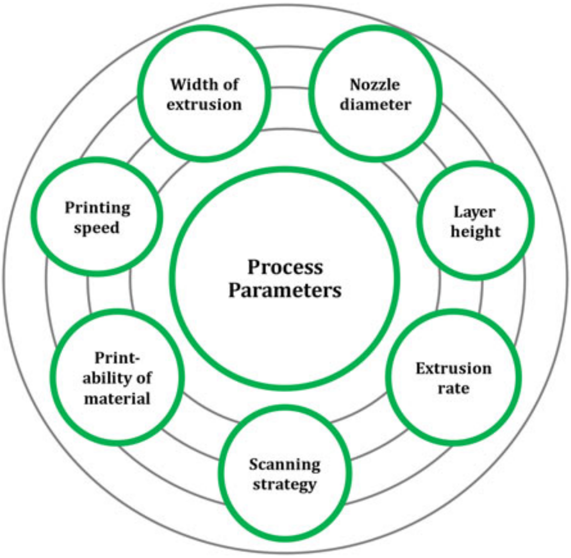
Process Parameters

Process parameters play a significant role in additive manufacturing processes to build defect-free parts [64, 65]. Hence, influence of the process parameters in 3DCP may hinder the quality of the structure. The primary process parameters used in 3DCP are shown in Fig. 5 [66]. Several researchers reported on the effect of process parameters on structural properties. Putten et al. 2018 [67] reported that 3D printing of Cementous material with equal and zero time gap of layers printing between the layers. In the case of zero-time gap between layers results in an equal distribution of porosity. In contrast, increasing the delay time (10–60 min) results in larger pores in the lower and center of the printed specimens. This can be attributed to the fact that the second layer induces less compaction on the layer underneath it, as its already hardened due to the influence of a 10–60 min of time gap. The zero-time gap and time gap effects on pores size are reported in Fig. 6. The specimens printed at a higher printing speed generated lower surface roughness than that of specimens produced at a lower printing speed. Hence, achieving a balance between the printing speed and surface roughness was specified to be the critical aspect.

Wolfs et al. 2019 [68] and Sanjayan et al. 2018 [2] reported the effect of surface moisture on interlayer bond strength via three different gap times (10, 20, and 30 min). It was found that the 3D printed layers of moisture decrease then increase, as shown in Fig. 7. However, the moisture level of the layers depends on the bleeding rate, evaporation rate, and printing process parameters. If the surface of the layer is dry, it results in poor interlayer bonding because of poor malleability.

Zareiyan and Khoshnevis 2017 [70] stated that interlocking layers increased bond strength by an average of 17% due to an increase in the contact surface. Kloft et al. 2020 [38] studied the inflence of interlocking of layers on the bond strength of

Fig. 5 Process parameters in 3DCP



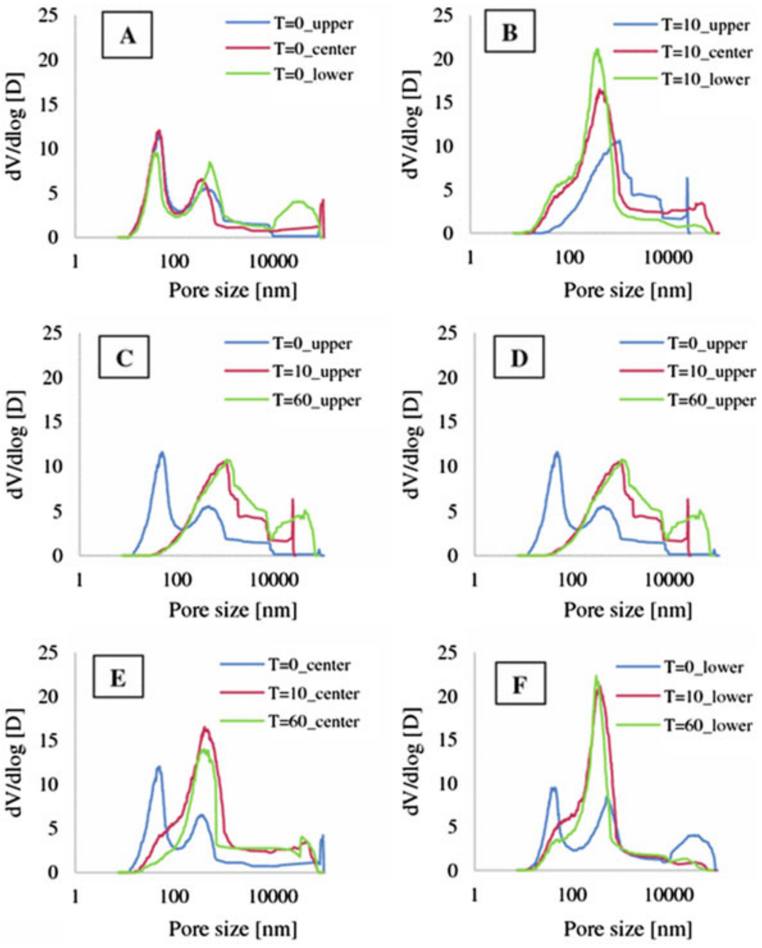


Fig. 6 The variation of pore size at zero and with different time gaps (Reproduced from [67])

structures. Contour-crafted specimens show that the bond strength is sensitive to the interlocking of layers. Tay et al. 2019 [69] studied the viability of changing the print parameters. The nozzle travel and volume flow rate significantly impacted the solidity ratio. The effects of flow rate and travel speed on print quality was observed. Senff et al. 2020 [71] reviewed the printing parameters' effect on the prints' quality. They concluded that a smaller nozzle could deliver good quality prints if the mixture has greater fluidity (avoids the clog in the system). Kruger et al. 2020 [72] developed a numerical model for determining the print speed and layer height combination, which gives a faster building rate and achieves the object's successful build. A case study has been done, and the optimal parameters determined a print speed of 87 mm/s and a layer height of 8 mm. The vertical building rate and time taken to print were determined to be 17.56 mm/min and 28.7 min, respectively.

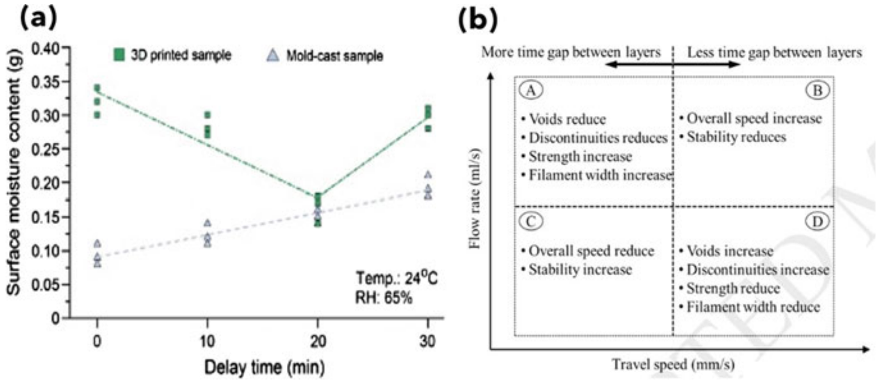


Fig. 7 3D printed and conventional mold-cast samples moisture level at different time gaps (Reproduced from [2, 68]) and effects of process parameters on prints (Reproduced from [69])

Sanjayan et al. 2021 [73] studied the effects of vibration on the print quality of concrete printing. It was found that the vibrations involved improved the material's extrudability, reduced the extrusion pressure, and improved the print quality by reducing voids and entrapped air. Babafemi et al. 2021 [74] researched to enhance bond strength in 3DCP. It was concluded that interlocking patterns recorded a 26% improvement in bond strength. An increase in the effective bond area increased the bond strength by 60%. Comminal et al. 2020 [75] conducted a computational fluid dynamics analysis of concrete printing. Layers were printed using a 25 mm diameter nozzle in an articulated robot system. It was found that the geometrical aspect ratio and the speed ratio significantly influenced the geometry. The printed layers varied from circular profiles to rectangular cross-sections with rounded corners. The side flow of the material is caused by the pressure applied on the extruder, leading to challenges in multi-layer printing. It can be concluded that the process parameters play a significant role in determining the quality of components. Optimum process parameters must be obtained prior to deposition via computational modeling or experimentally. The following section discusses the applications of 3DCP.

5 Applications of 3DCP

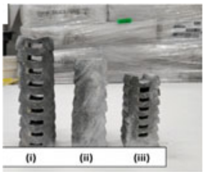
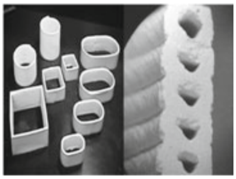
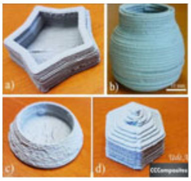
The first exploratory application of 3DCP was reported by Pegna in 1994 [26]. Later 2004, Prof. Behrokh Khoshnevis of the University of Southern Carolina demonstrated the first 3D-printed wall [76]. After that, 3DCP was revered in many construction and building applications, including relief shelters, canals, living houses, metal frames for solid structures, micro homes, cyclists bridges, NASA outer space applications, asphalt roads, complex structures, and others [26, 27, 31, 71, 76–78]. Table 1 presents the applications in architecture, construction, and building sector.

Table 1 Applications of 3DCP in construction and building industry

Authors name, reference, and journal	Applications/materials	Methods	Products/components/ samples
Joseph Pegna 1997 [26] Automation in Construction	Construction, large structures, multimodal structures/sand and Portland cement	Additive manufacturing, rapid prototyping, solid freeform fabrication	 Steamed cement-silica of HO-scale block-house
Paolini et al. 2019 [66] Additive Manufacturing Journal	Construction, bicycle bridge, building components, footbridge/ aggregate-materials, reinforced steel, carbon fiber-reinforced ABS components and	Concrete extrusion, powder bed processes Wire arc additive manufacturing (WAAM)	 Massachusetts Institute of Technology construction printer
Valente et al. 2019 [31] Journal of Composites Science	Architectural and construction sectors/ cement-based sandwich-waste tire rubber aggregates, rubber-concrete	Robotic arm, gantry systems, contour crafting	 3DCP of bathtub
Dezeen 2017 [78]	Concrete bridge-cyclists/ concrete	Extrusion-based robotic arms	 Concrete bridge

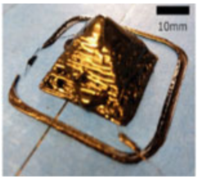
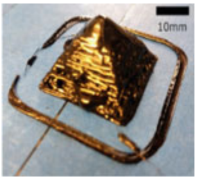
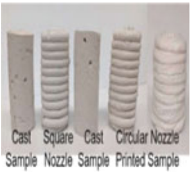
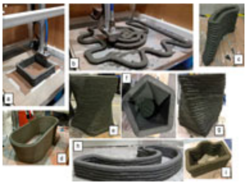
(continued)

Table 1 (continued)

Authors name, reference, and journal	Applications/materials	Methods	Products/components/ samples
Ramakrishnan et al. 2021 [79] Cement and Concrete Composites	Construction industry/ ordinary portland cement (OPC) with cement (AS 3972-Type GP) and fine/TGS silica sand	Filament extrusion technology	 3D printed wall (i) Hollow core (ii) Solid core (iii) U-shape
Khoshnevis et al. 2006 [30] International Journal Industrial and Systems Engineering	Residential housing units and civil structures/polymer, ceramic slurry, cement	Contour crafting	 Contour crafted components
Ingrid Paoletti 2017 [80] Procedia Engineering	Multi-performative building components/ clay	Robotic arms-based 3D printer	 Printed clay components
Carlos et al. 2019 [57] Processing and Application of Ceramics	Construction/kaolinite clay with small additions of lime, fly ash and talc ceramic powders	Direct ink writing (DIW) 3D printing technique	 DIW printed with clay wall with fly ash of different geometries

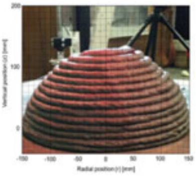
(continued)

Table 1 (continued)

Authors name, reference, and journal	Applications/materials	Methods	Products/components/ samples
Amy Fearson 2016 [81] Dezeen	Micro home/bioplastic	Extrusion based FDM	 3D printed microhome
Perrot et al. 2020 [53] Materials	Concrete structures/ cement CEM I 52, limestone, kaolin clay, river sand	Extrusion-based 3D printer	 Screw extrusion fabricated bending samples
Jackson et al. 2018 [48] Materials and Design	Roads, pothole repairs/ Asphalt, Bitumen	Extrusion-based 3D printer	 Printed pyramid
Manikandan et al. 2020	Civil infrastructures/ clay	Direct ink writing (DIW)	 Printed various parts
Tay et al. 2017 [3] Virtual and Physical Prototyping	Building and construction/clay, cement, ceramic, chopsticks, cementitious, viscous materials	Contour crafting, 3D concrete printing (gantry 4 axis/6 axis), Binder jetting	 3DCP of various prototypes

(continued)

Table 1 (continued)

Authors name, reference, and journal	Applications/materials	Methods	Products/components/ samples
Bester et al. 2019 [72] Proceedings of the fib Symposium 2019 Concrete—Innovations in Materials, Design and Structures	Construction industry/ 579 kg of Cem II/A-L 52.5 cement, 165 kg of fly ash, 83 kg silica fume, 1167 kg of local, natural sand, and 261 kg of water per cubic meter	Gantry-type 3D concrete printer	 3D printed benchmark structures
Muthukrishnan et al. 2021 [32] Cement and Concrete Composites	Construction/concrete, geopolymer	3D concrete printing	 Articulated complex column
Mechtcherine et al. 2019 [29] Automation in Construction	Construction, building and architecture/ concrete or mortar	On-site extrusion-based digital construction (EBDC)	 Extruded coarse and fine layers
Buswell et al. 2018 [17] Cement and Concrete Research	Large-size construction/concrete or mortar	3D concrete printing	 In-situ printed columns and walls

(continued)

Table 1 (continued)

Authors name, reference, and journal	Applications/materials	Methods	Products/components/ samples
Jipa et al. 2019 [25] SCF'19: Symposium on Computational Fabrication	Formwork for stairs/ concrete	Extrusion based 3D-printer	 Topology optimized stair case
Gaudillière et al. 2019 [24] 3D Concrete Printing Technology	Lost formworks structures, pillars, and an interior separation wall for the house, rain collection tank/ concrete	Large scale extrusion based 3D-printer	 Assembled 3D-printed concrete formwork filled with UHPC casting  Interior wall made of the 3D-printed concrete formwork filled with cast concrete after finishing
Lin et al. 2022 [23] Automation in construction	Concrete arches and vaults/concrete	3DCP robotic arm and a reconfigurable print bed	 Assembled 3D printed Concrete arch
Ishan Patra The Hindu 2022 [77]	Metal bridge-pedestrians and cyclists/stainless steel	Six axis robotic arm equipped with welding gear	 Metal bridge

6 Challenges and Prospects

The based on the available literature on construction and building applications of 3DCP. The following challenges and prospects are identified:

- 3DCP offers design freedom and automation of the entire construction process. However, large build volume, hardware, equipment's related issues need to the investigated;
- 3DCP is building the houses layer-by-layer. Therefore, real-time build monitoring systems (using a real-time video camera, pyrometer, thermal camera, etc.) for human safety, bead size, and deformation analysis are to be developed or innovated;
- Large-scale construction is enabled via 3DCP without the use of formwork. However, layer-by-layer deposition of concrete results in voids and dwell time between layers hinders mechanical properties, especially the durability of materials;
- The computational modeling of the concrete printing process for concrete, metals, polymers, and composites has been reported to understand and prevent build failures due to large deformation and residual stresses. However, computational methods are expensive and time-consuming as they involve multi-scale and multi-physics mechanisms. The significant opportunities to address comprehensive building process simulation and validation against the experimental data of 3DCP parts;
- Presently 3DCP have work envelope constraint, hence challenging to build a multi-story building simultaneously;
- The complete construction and building project involve foundation, building, post-processing, and maintenance stages. Therefore, its mandate is to assess the cost estimation and building performance with respect to the lifecycle of the 3DCP project; and
- The cybersecurity and intellectual property right of CAD files of buildings/ products is a cause of concern. Otherwise, since reprography is easy, it would be resold to others; therefore, the high potential of framing the standard practices for the construction and building via 3DCP is essential.

7 Conclusions

Three-dimensional concrete printing (3DCP) is an automated construction process. It would eliminate the labor necessary for building and construction. Concrete is a commonly used material in the construction and building industry. Concrete material with suitable properties is required in 3DCP, leading to proper extrudability, printability, and hardenability. The process parameters play a significant role in building defect-free components/walls. Hence, process parameters in 3DCP may hinder the quality of the structure. The process parameter optimization was carried out via experimentation or computational modeling. The 3DCP is revered into constructions and building applications, including relief shelters, canals, living houses, metal frames for solid structures, micro-homes, cyclist's bridges, NASA outer space applications, asphalt roads, and complex structures. Therefore, 3DCP has a lot of latent in building and construction applications. Presently research/experimentations are going on, and it requires widespread interest to develop the technology for the full fledge building capability.

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Chapter 13
Applications of Additive Manufacturing in Biomedical and Sports Industry

Shrishail B. Sollapur, P. C. Sharath, and Pratik Waghmare

Abstract The fabrication of fully functional active components via additive manufacturing, also known as 3D printing, has progressed beyond mere prototype. With composites, metals, ceramics, concrete, and polymers, it is a flexible production technique. This article focuses on the evolution of additive products in the biomedical and sports industries. Additionally, a number of instances of additive manufacturing techniques used in the creation of unique goods are provided. The use of additive manufacturing as a collaborative tool with the idea of innovative problem-solving techniques in the creation of new items has also been given a conceptual framework.

Keywords 3D printing · Titanium · Cobalt · Shape memory alloy · Biomedical and sports industries

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1 Introduction

A novel approach to traditional manufacturing techniques is additive manufacturing (AM). In traditional manufacturing methods, parts are created by eliminating undesired components from raw materials before converting them into finished products. The amount of material wasted with this process is substantial, and fabricating complex pieces is challenging or time-consuming. AM is frequently referred to as 3D printing, a process that overhauled the manufacturing sector. In this method, which is known as additive manufacturing, parts are created by putting a layer on top of another [1]. Rapid prototyping, on-demand manufacturing, digital fabrication, desktop manufacturing, layer manufacturing, direct manufacturing technology, and 3D printing are other names for additive manufacturing [2]. Stereolithography (SLA), digital light processing (DLP), selective laser sintering (SLS), electron beam melting (EBM), fusion deposition modelling (FDM), multijet/polyjet 3D printing (M/P 3D printing), selective laser melting (SLM), and laminated object manufacturing are a few examples of additive manufacturing processes (LOM). These procedures involve the utilisation of a wide variety of materials, including ceramics, plastic, metal, liquid, powder, and even live cells [3].

It has drawn attention because of its simplicity in fabrication, limitless design potential, low level of complexity, decreased part count, weight reduction, and increased system effectiveness. With such a response, AM revenue was previously anticipated to be $2.7 billion; nevertheless, it will increase to almost $100 billion over the next twenty years [4]. It has demonstrated promising results in the biological sciences, industrial applications, aeronautical technology, and academic research. This technique is applied to the aerospace industry to boost system efficiency overall, reduce part weight by reducing the number of parts, and increase fuel efficiency, which in turn affects cost [5].

Additive manufacturing, which enables the printing of customised body parts with intrinsic geometry and offers each patient a unique set of treatments, is quickly revolutionising the medical sectors. AM has developed over the last few decades into a flexible and useful technique for creating geometrically challenging structures in the medical sector. Dental implants, heart valves, joint replacements, cranial plates, spinal fusion cages, valve, stent, and knee implant pieces have all been created using additive manufacturing technology. However, in the medical field, 2D radiographic pictures from CT scans, MRIs, and X-rays can be transformed to 3D digital print files, enabling the construction of specialised anatomical, intricate, and clinical structures [6].

To create a computer-aided design (CAD) model, software is used. The model is then transferred via slicing software in the subsequent step to produce a format for its layered representation known as Standard Tessellation Language (STL) [7]. To begin printing, the STL file is loaded onto a 3D printer. Immediately following printing, the part is sent for post-processing, where it is essential to clean it, remove it from the build plate using electric discharge machining (EDM) [8], and then heat

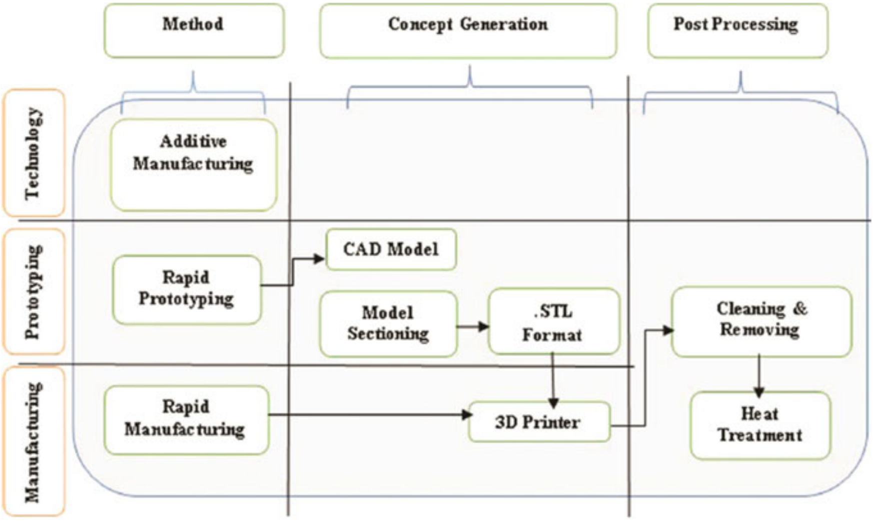

Fig. 1 Schematic of processing steps in AM [9]

the substrate in a furnace to relieve internal stresses. The numerous manufacturing processes stages are shown in Fig. 1.

Objects made from a variety of metals, polymers, ceramics, photopolymer resins, and wax grades have been created via 3D printing. Because raw materials are handled substantially differently than they would be in a regular production method, materials are crucial to the additive manufacturing process. As a result, it is now easy to transition from traditional to additive manufacturing. The seven primary approaches used in the AM process were categorised by the American Society for Testing and Materials (ASTM F42). Fused deposition modelling, often known as material extrusion (ME), is a method that employs plastic and polymer-based wire filament as its raw material (FDM). The form of the spool-wrapped wire serves as the primary raw material for this technique. Fused layer manufacturing (FLM) and fused filament fabrication are other names for the FDM process (FFF) [9]. Binder Jetting (BJ), also known as 3D inkjet technique, adheres one layer of a particle on top of another using liquid binders. To create different grade objects, multi jetting (MJ) sprays a liquid photo-reactive chemical over a construction platform [10]. In order to make a polymer product (DLP), stereolithography (SLA) and digital light processing (DLP) both used a vat of liquid photopolymer [11]. Sheet lamination is the mechanical bending of sheets or foils to join or laminate them (SL) [12]. A technique called direct energy deposition (DED) uses a laser beam and powder to construct structures at the same time. Typically, wire-feed and powder-fed systems are the foundation of the DED process [13]. Powder bed fusion (PBF), the fourth frequently employed technique, involves inserting material in the form of powder into a platform that has been built using a powder recoater system. The energy source used to scan the geometry for the melting of the powder is a laser beam.

Healthcare is expected to alter as a result of additive manufacturing, which has recently shown tremendous potential in the medical sector. Some of the most frequently used applications of additive manufacturing include the creation of tissue and organs, anatomical models, the development of specialised prosthetics and implants, advancements in the pharmaceutical industry, particularly with regard to drug dosage forms, discovery and delivery, and other biomedical applications [14]. Due to its many benefits, including the ability to customise and personalise medical products, biocompatibility, cost effectiveness, increased productivity, accessibility, quick production times, simple assembly, collaboration, and democratisation, additive manufacturing is widely used in the medical industry [15]. However, additive manufacturing is still not widely used due to its slow uptake in industrial production [5].

But in the medical industry, where highly precise and tailored products are needed in smaller quantities, this limitation is seen as a benefit. This is because each patient has different needs for medication and individualised treatment. As a result, clinical and biomedical applications are where additive manufacturing is best suited and most frequently used [16]. Researchers are now exploring for bio-comparable materials to produce vascularized people after several have attempted to map human organs and transform them into virtual three-dimensional creations. There are still certain regulatory and scientific challenges to be solved, nevertheless [15]. Figure 2 depicts the distinct stages needed to build the 3D medical models. Images are acquired, or the structural target area is chosen, three-dimensional geometry is evolved through processing of the medical images, materials and three-dimensional printing equipment are chosen for implants, post-processing is applied as needed, testing is done, and finally the implant body is implemented. A better grasp of diseases, their costs, the surgical procedure, the use of surgical instruments, and the design of implanted devices that are patient-specific are just a few examples of how medical models can improve a surgeon’s knowledge and skill [17]. Custom fit masks, the development of novel organs, and surgical practise, among other things, are best served by medical additive manufacturing [18].

The market for sporting goods is now utilising additive manufacturing. Due to the market’s strong emphasis on customer perception, the advantages of unique items and customisation made available by additive manufacturing may be crucial. Because every human’s anatomy is programmed differently, each person has different preferences for fit and form. The equipment that players often use in sports, such as a racket with greater grip, a suit with better aerodynamics, or a cleat with higher traction, has a significant effect on their performance. In addition, the right equipment can prevent accidents, whereas the wrong equipment can easily result in injuries. Companies are continuously challenged to develop new goods that surpass those of the competition and offer a good fit and performance in the fast-moving sports market. However, many goods in the sports equipment sector are now mature and hardly have room for improvement.

AM provides the chance to create products that are fully tailored to match individual structure and performance needs, potentially enhancing comfort, reducing injuries (especially overuse problems), and enhancing performance. Notably, the

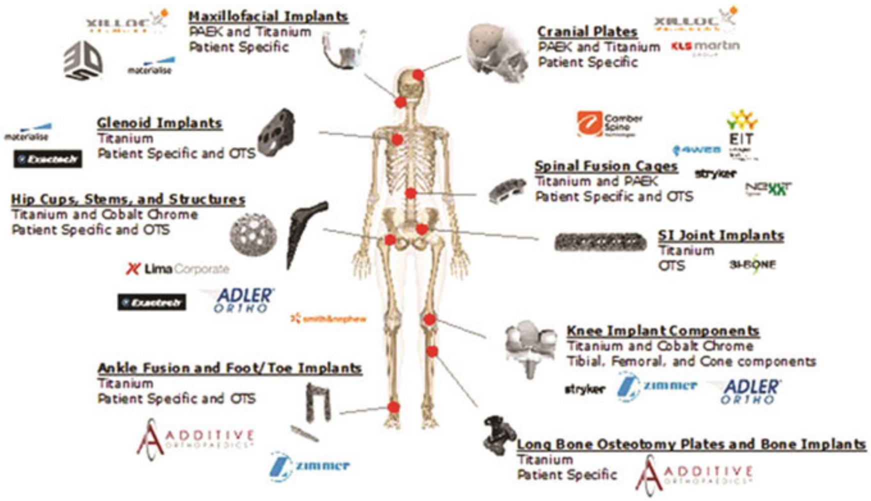

Fig. 2 AM used for orthopaedic implants [19]

sparse amount of sports AM research that is now available rarely provides goods with thorough case studies or statistics, despite the fact that [20] claim that the acceptance of sports business is just in the "initiating phase." The 2019 research by Meier et al. on AM awareness in the sports industry Despite signs that additive manufacturing is being more widely used in other sectors, the aforementioned restrictions—such as a scarcity of usable materials, a lack of expertise in designing products for additive manufacturing, and expensive equipment costs—remain obstacles. The study also found that, although rapid prototyping, a term used to describe the application of AM technologies for producing prototypes rather than finished products, helps to drive innovation in product design, it is not being significantly used to enhance the production of new products. This is because the sports industry lacks a general understanding of additive manufacturing (AM) technology.

The sporting uses of 3D printing that have received a lot of attention recently include shoes by Nike, Adidas (such as Future craft 4D14) [20], and New Balance (such as Zante Generate), as well as shin pads, bicycle helmets, Olympic speed skating gloves, prosthetics used in the Paralympics [21] and countless other examples. Carbon (Redwood City, CA, USA), the inventor of Continuous Liquid Interface Production (CLIP) technology, has created three famous sports products that are either already on the market or will be in the near future [22]. These products include the S-Works cycling seat, the Adidas Future Craft 4D footwear, and a football helmet liner that can be customised (Des Plaines, IL, USA). The Power Saddle for Specialized has a lattice construction with more than 14,000 struts (Specialized Bicycle Components, Morgan Hill, CA, USA) [23]. Although it's possible that these instances of AM acceptance in the sports sector are the exception rather than the rule, their popularity online and rising consumer awareness do point to a growing market readiness to accept new performance-driven features.

Due to the rapid rate of AM invention, information regarding new shoes and other AM-produced products is frequently only accessible through company media releases and websites for mainstream news outlets rather than more established academic sources. This issue has been highlighted, especially within formal AM education, where project-based learning and flipped classroom formats encourage the use of numerous digital resources to support learning that is up-to-date and industry-aligned [24]. Given these disparate depictions of AM in sports, this study looked for any accessible scientific proof that AM results in better sporting goods. The main objectives were to describe the various AM-related digital technologies, materials, software, and equipment used, to document the scope of research investigations, to summarise the prospects and constraints of AM from the literature, and to list the different sports and products that use AM.

The objective of review paper is to compile work of numerous research's in the field of additive manufacturing, with a particular emphasis on applications in the medical and sporting industries that make use of diverse AM technologies and materials. This review article might end up carrying the research in this field into the future.

2 Manufacturing Methods for Biomedical and Sports Industry Using Additive Manufacturing

2.1 Biomedical Applications Using Additive Manufacturing

The primary materials used in the production of contemporary medical implants are ferrous alloy steel, cobalt-chromium-based materials, and titanium-based materials. Additive manufacturing (metal-AM) is one of the modern fabrication processes used to provide bespoke characteristics that satisfy structural requirements. Figure 3 illustrates the usage of biomaterials manufactured by additive manufacturing technology used in different parts of human body.

Currently, Metallic biomaterials are currently used in the production of various biomedical devices. This section discusses the use of various AM techniques and the impact of different processing parameters.

2.1.1 Titanium Alloys

AM of individual materials is popular in the titanium market titanium metal matrix composites and titanium-based structures for use in biomedical applications. The titanium metal matrix composites are given special attention in a distinct subsection

Fig. 3 The schematic depiction of the biomedical application of additive manufacturing of biometals includes the cranial prosthesis, dental implants, acetabular cup, interbody fusion cage, hip prosthesis, and knee prosthesis [25]

because to their significance. Ti-based materials have shown to be very biocompatible. They also exhibit outstanding resilience to corrosion and fatigue stress. Additionally, Ti-based alloys are lighter than other metallic materials due to an inherent high strength to weight ratio.

Furthermore, there are a number of drawbacks to materials made of titanium. Tribology-wise, Ti-based materials perform poorly. The limitations of Ti-based materials' mechanical properties are the cause of this issue. Ti-based alloys are frequently utilised for implants that must support weight, including total hip or total knee replacements. A strong bond between the new implant and the human tissue is crucial in these conditions. It has been shown that a layer of hard tissue slowly develops on the Ti implant. In light of this, there are still problems that need to be resolved even though Ti-based materials are a well-established materials system for use in biomedical implants. Utilizing additive manufacturing techniques can aid in resolving some of these problems. These options include creating porous or structurally graded components to promote bone regeneration as well as altering the surface of Ti-based materials to enhance their wear performance.

Kelly et al. used the Laser Additive Manufacturing (LAM) system of AeroMet Corporation to explore the micro-structural and thermo modelling of laser-produced Ti64 alloy [26]. Similar to earlier finds, researchers found -Ti laths with -Ti grains around them. There were many of equiaxed -Ti grain colonies in each of these bands. The LAM-deposited Ti64 alloy tested by Vicker as a microhardness sample has a hardness of roughly 350 HV. Porous Ti structures were shown using LENSTM by Balla et al. and Xue et al. [27]. The key to producing porous Ti components in this work was partial feedstock powder melting, in contrast to other attempts at processing Ti-based materials, which employed whole feedstock particle melting and solidification.

According to this theory, the central cores of the powder remained unaltered and only the exterior surfaces were melted, creating the porous structures depicted in Fig. 4 [28]. Particles bonded to one another as a result of these melted surfaces, and any remaining porosity was also created. Additionally, finished components displayed a Young's Modulus that was comparable to that of genuine bone [29]. The porous Ti produced by LENSTM has better biological characteristics than bare Ti plate, as illustrated in Fig. 4, according to in vitro analyses [27].

Direct Electron Beam Melting was used by Heinl et al. to fabricate cellular Ti structures [30]. Ti64 powder was used to create the structures, which were then vacuum-fabricated at a pressure between 10–4 and 10–5 mbar to eliminate any potential oxygen or nitrogen contamination. Samples with three distinct porosities—25%, 38%, and 60% by volume—were effective in each of the three attempts to generate connected porous structures.

Harrysson et al. demonstrated how to employ EBM to produce Ti64 structures with densities ranging from 4 to 40%, and then used the 3P bend technique to assess their flexural and compression strength. It was shown that the compressive strength dropped when cell size or structural porosity increased. A few examples of these EBM-processed structures are shown in Fig. 5 [31]. Structures with a cell size of 3 mm and a relative density of 0.41 had a compressive strength of 85.72 MPa, whereas structures with a cell size of 12 mm and a relative density of 0.04 had a compressive strength of 0.84 MPa.

Ti-based materials that are dense and porous have been processed using selective laser sintering (SLS) or selective laser melting (SLM) for use in biomedical applications. Hot isostatic pressing (HIP) and SLS were used by Das et al. to manufacture net forms of Ti64 alloy [32]. To create a 92% dense component, Ti64 powder was first selectively sintered with a laser source. The part's density was greatly raised during HIP post-processing. Since the pieces made in this way were almost net-shaped, more machining was required. From the exterior to the interior, the micrographs of SLS/HIP treated products apparently change. While the bulk microstructure was made up of coarser grains, the skin or outer walls displayed a fine Widmanstatten structure with a high aspect ratio of the lamellar phase. A temperature gradient created by the surface melting of powders was thought to be the cause of the disparity in

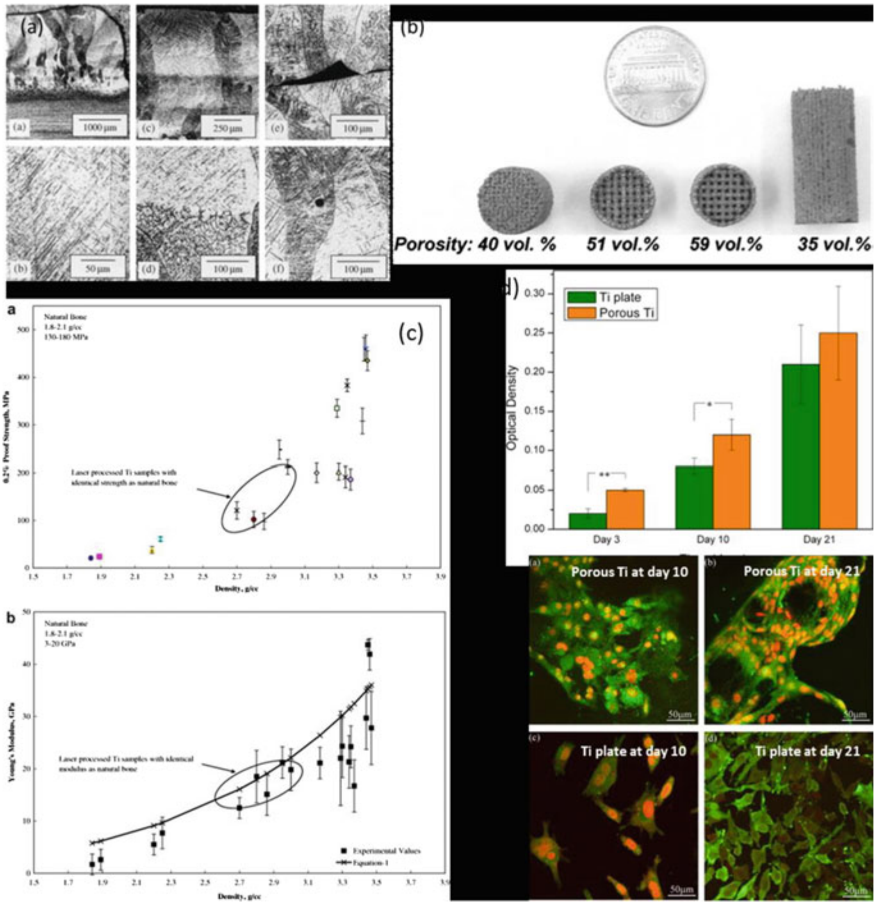

Fig. 4 **a** The Ti-6Al-4V alloy's general microstructure, produced by laser additive manufacturing [29]. **b** Porous Ti structures that have undergone LENSTM processing; **c**-**a** the impact of density on 0.2% proof strength; and **c**-**b** a study of the porous Ti samples' effective moduli as calculated empirically and theoretically [27]. **d** Ti plate and porous Ti were seen using confocal microscopy on days 10 and 21 as well as during MTT assays on days 3, 10, and 21

microstructure. A sub-scaled replica of an AIM-9 Sidewinder missile housing component was produced to show the viability of the SLS/HIP process. This component's microstructure was completely dense.

Fisher et al. also demonstrated the sintering of Ti powder. Ti64 components were produced by Hollander et al. using SLS or DLF (Direct Laser Forming) technology, and they were then tested on vitro with consideration of human primary osteoblast cells. Figure 5 [33] shows the procedure the authors used to verify the feasibility of SLS/DLF component manufacturing. The DLF pieces' unpolished surfaces had a granulated appearance, necessitating finishing work. Nominal pore

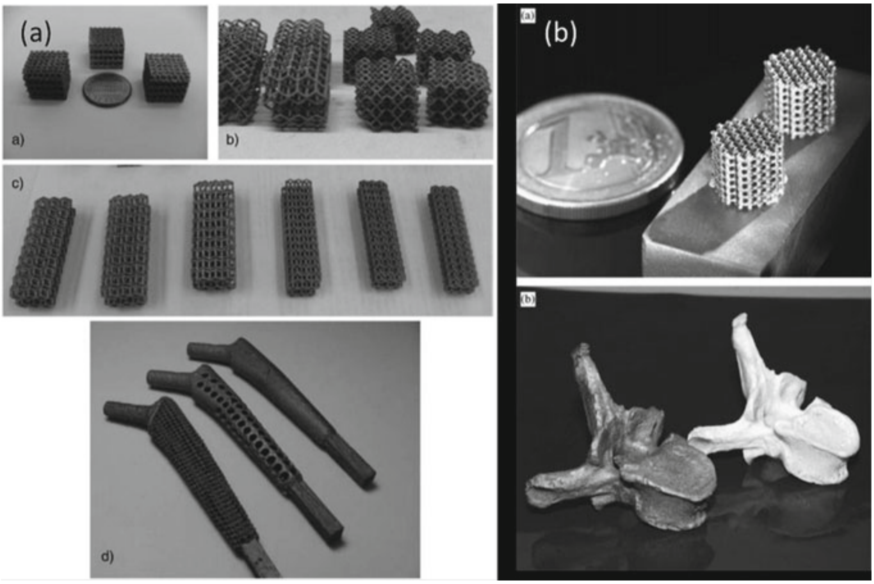

Fig. 5 Shows various Ti-6Al-4V assemblies created using the E-grin melting method [31] in (**a**) and mesh Ti64 alloy assemblies and a model of a human vertebrae created using the SLS/DLF approach (**b**)

sizes for porous components ranged from 500 to 700 m, and most pores were cylindrical in character. The SLS/DLF items' mechanical characteristics considering the strength of 1200 MPa tensile & an 6.5% deflection. Elongation at failure doubled to 13.0% following post-process annealing heat treatment, which also decreased tensile strength to 1042 MPa.

Results from in vitro tests showed that the materials were not harmful. The authors cultured cells in vitro on porous materials with 500 m, 700 m, and 1000 m average pore sizes. After 14 days, samples with 500 m hole diameters demonstrated the best interactions between cells and materials. Kruth et al. worked on the comparative wear characteristics for several materials created using the SLS/SLM process. Several materials tested on fretting wear tests with weights of 2 N and 6 N, and damages on the wear was calculated as mm^3 of material lost over 10×10^3 cycles [34]. At 2.1 N load, Ti64 alloy has a wear volume of 7.362×10^3 mm^3, while at 6 N load, it has a wear volume of 9.337×10^3 mm^3. For 2 N and 6 N stresses, the damages for the CoCrMo alloy were 1.474×10^3 mm^3 and 2.252×10^3 mm^3.

Three-dimensional (3D) fibre deposition, which was initially intended for 3D manufacture of polymeric components, is another technique for treating porous Ti-based materials. In the scaffolds created by 3D fibre deposition, Li et al. revealed the aspect of bonematerial interaction [35]. A slurry was pumped via a syringe in a Bioplotter device using Ti64 alloy powder and 0.6% aqueous methylcellulose solution. A complete 3D scaffold is created through such layer-by-layer deposition and is afterwards sintered for two hours at 1200 °C. These samples ranged in porosity from 39 to 68%, while the diameters of the square and rectangular pores ranged from 200 to 800 m. After that, samples were placed inside the lumbar goat spines for in vivo testing. After a year, animals were sacrificed.

No sign of toxicity or inflammation were present. Even when the implant's porosity and pore size grew, the amount of new bone formation increased. Additionally, Ryan et al. used wax models manufactured on a Thermojet 3D printer to create porous Ti scaffolds [36]. The wax mould was filled with a Ti powder and ethylene glycol slurry, which was then dried. The Ti structure was sintered between 1100 and 1300 °C in a vacuum after the wax had been removed. These sintered Ti scaffolds were used to cultivate SAOS-2 pre-osteoblast cells for more than 3 weeks without any issues of toxicity. These have a average pore size of 465 170 m and a porosity of 45%. Additionally, scaffolds with pore diameters of 200, 300, and 400 m with a porosity of up to 66.9% were created.

LENSTM was used to treat Ti-TiO_2 compositionally graded structures [37]. TiO_2 content was raised from 50 to 90%. The inclusion of 50% TiO_2 in Ti led to a hardness of 1100 HV. LENSTM has also been used to strengthen SiC in Ti [38, 39]. With a hardness of up to 1000 HV, the Ti substrate's tribological performance was increased by more than an order of magnitude. Through nitrogen injection in the oxygen free-argon rich chamber with LENSTM operation, Zhang et al. demonstrated the formation of nitrides of Ti and Si on Ti substrates. This technique is a relatively new way to create an in-the-moment ceramic phase [40]. The surface of Ti was then coated after being fed a combination of Ti and Si powders. The resultant structures had an alpha Ti matrix and were composed of dendrites of TiN and Si3N4. These in-situ produced ceramic coatings ranged in hardness from 1300 to 2100 HV and were 200 times more resistant to wear damage than a Ti substrate.

2.1.2 Cobalt Alloys

Understanding the viability of these materials in bulk form is crucial from the perspective of biomedical applications. Medical grade CoCrMo alloy was demonstrated by Janaki Ram et al. using LENSTM-based additive manufacturing [41]. LENSTM 285 W laser power was used to treat samples that were 6 mm thick. Each layer's microstructure was made up of very small equiaxed dendrites and slightly coarser columnar dendritic phase. These changes in the solidification circumstances led to these microstructural variances. It was also noted that the equiaxed and columnar dendritic sections contained carbide phase. The carbide layer was either solitary particles or a resilience network in the interdendritic zones. The CoCrMo alloy utilised in LENSTM technology has a hardness of 40 HRC, which is comparable to the hardness of 41 HRC of the wrought base. The abrasive wear resistance was found to be below that of the substrate. The peculiar morphology of the carbide phase, which was predominantly present as thin and long connected particles rather than being noticeably more regular, spherical, and equally dispersed across the treated substrate, is credited by the researchers as the cause of this.

E-beam melting has also been used to create dense, porous co-based alloys [42]. Figure 6 displays a number of test specimens and joint replacement components made utilising the E-beam technique. CoCrMo alloys having a density of 8.4 g/cm^3 were treated to produce completely dense components. Additionally, components for open cellular mesh and femoral knee implants were produced utilising an electron beam-based additive manufacturing technique. The usual ASTM F75 CoCr alloy treatment and annealing heat treatment were also applied to the components of the femoral knee implant as they were being manufactured. The microstructure of fully dense components revealed columnar grains, arrays of carbides, and zigzag carbide phases.

The average hardness in the horizontal plane was 4.4 GPa for a rectangular shape of fully dense CoCrMo alloy treated in an E-beam and 4.7 GPa for a cylinder specimen. These specimens were made with CoCrMo powder, which is around 30% harder than these hardness ratings. The prototype femoral knee component's microstructure was made up of columnar carbides and arrays of carbides that ranged in size from 2 to 3 m. As demonstrated in Fig. 7, the microstructure of polished and annealed femoral components revealed an intergranular fcc structure with observable annealing twins and finer carbide phases. The CoCrMo alloy's struts in the reticulated mesh structure resembled totally dense block and cylinder samples in terms of their microstructure. The hardness of the struts was 6.8 GPa in the horizontal plane and 5.6 GPa in the vertical plane, which was about 25% greater than that of the dense structures.

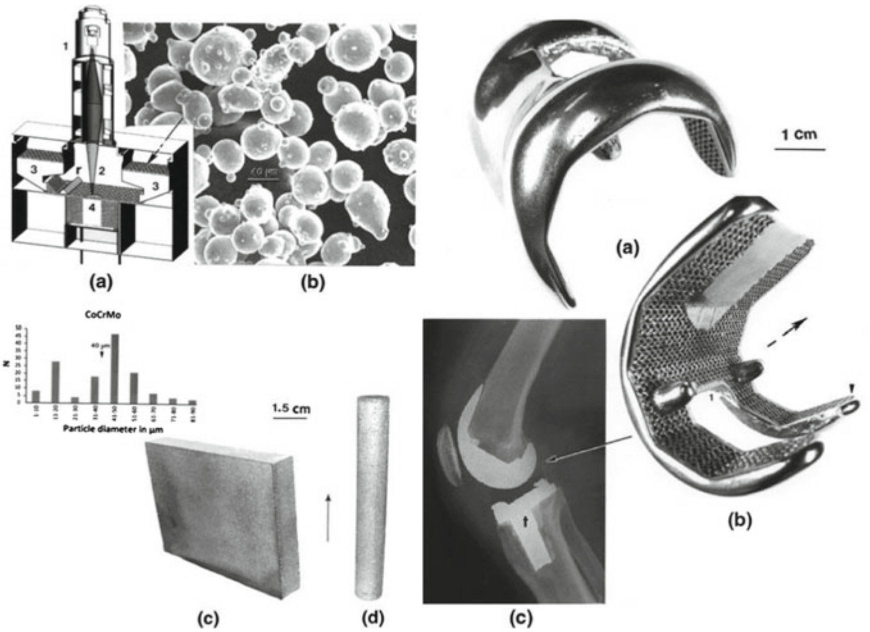

Fig. 6 E-beam treated porous femoral knee replacement component and dense CoCrMo alloy [42]

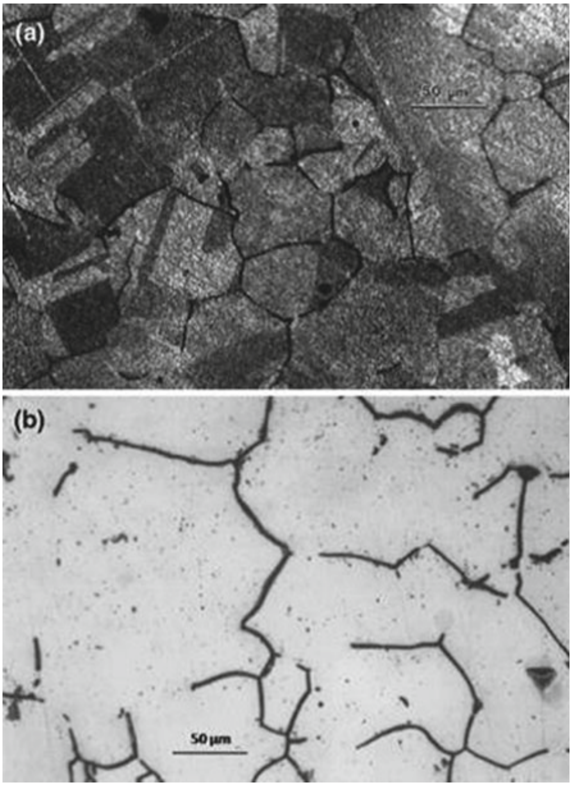

Fig. 7 Microstructure following E-beam processing and annealing [42] depicts annealing twins in CoCrMo

2.1.3 Shape Memory Alloys

Recently, there has been an increasing interest in using these smart materials in the biomedical sectors of tissue engineering, drug delivery, endovascular surgery, orthodontics, and orthopaedics. Biomedical polymers must be produced from highly biocompatible and nontoxic components in order to function without inducing immune-inflammatory responses. Their biodegradability/biostability, mechanical characteristics, and activation processes are additional factors to be taken into account while constructing biomedical SMPs. The high-temperature SMPs, which have transition temperatures close to that of the body (37 C), are the activation methods that have generated the greatest study on polymers for biological uses [43]. Medical implants won't perform as well if biomedical SMPs are used at varying temperatures above or below body temperature. In order to circumvent this issue, the SME may also be activated remotely utilising apparatus such as infrared (IR), laser, ultrasound, etc. [44]. Other strategies exist, such as adding magnetic nanoparticles and functional fillers to the polymer matrix, which enables the implanted device to be activated inside the human body at the right temperature and position with the help of an external magnetic field.

According to their adaptable physical and mechanical qualities, aliphatic polyester-based SMPs are frequently utilised for a variety of biomedical applications, including resorbable implants, sutures, and wound closures [45]. SMPs are used in biodegradable smart sutures, which are used to close wounds (Fig. 8a) [46]. The right amount of stress must be applied to the wound margins for optimal primary wound closure, which has long been a major challenge in endoscopic suturing [47]. Applying larger strains will cause the knot of the suture to be secured by tissue necrosis, whilst employing weaker forces would cause the formation of scar tissue and possibly hernias. Lendlein and Langer [48] were the first to propose a disposable smart thermo-plastic suture based on oligo(e-caprolactone) diol as a viable remedy for attaining optimal wound healing in endoscopy treatment. This suture can be tied inside the wound, then extended outward with controlled force before being shrunk and tightened inside the body (Fig. 8a).

Self-fitting tissue scaffolds might be developed to treat abnormally shaped bones because of the special properties of SMPs. A PCL diacrylate-based SMP scaffold that can accommodate a craniomaxillofacial bone abnormality was created by Zhang et al. [49] (Fig. 9). When heated over Trans, the scaffold initially became pliable and mushy (55 C). Next, a model defect was hand jammed into the scaffold. The structure was enlarged to accommodate the crooked shape once the force had been released. After cooling, the scaffold became firm once more, and it was eventually sealed inside a typical flaw.

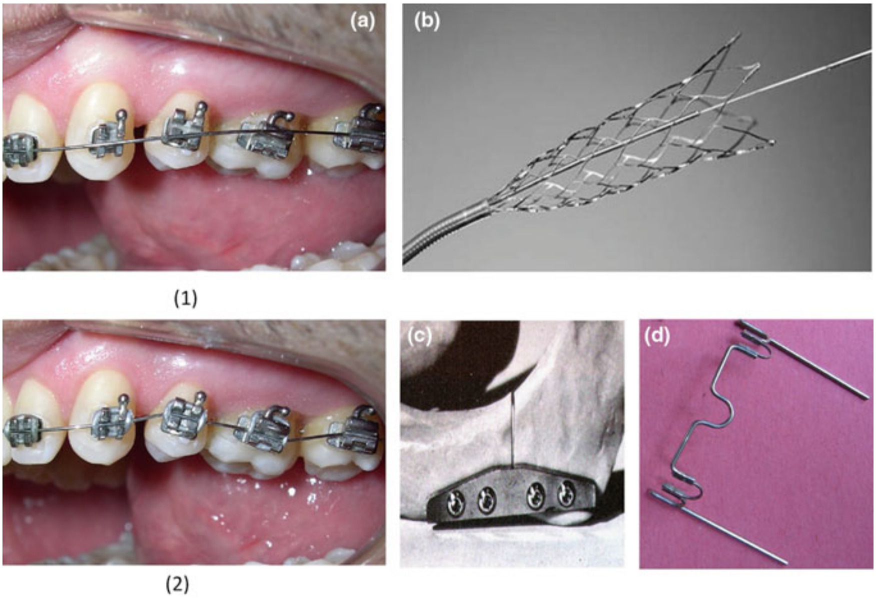

Fig. 8 Examples of typical NiTi biomedical applications: **a** orthodontic NiTi archwires (1) before and (2) after bracket engagement [46]; **b** NiTi self-expandable neurosurgical stent; **c** NiTi plate for mandible fracture; and **d** NiTi palatal expander [47]

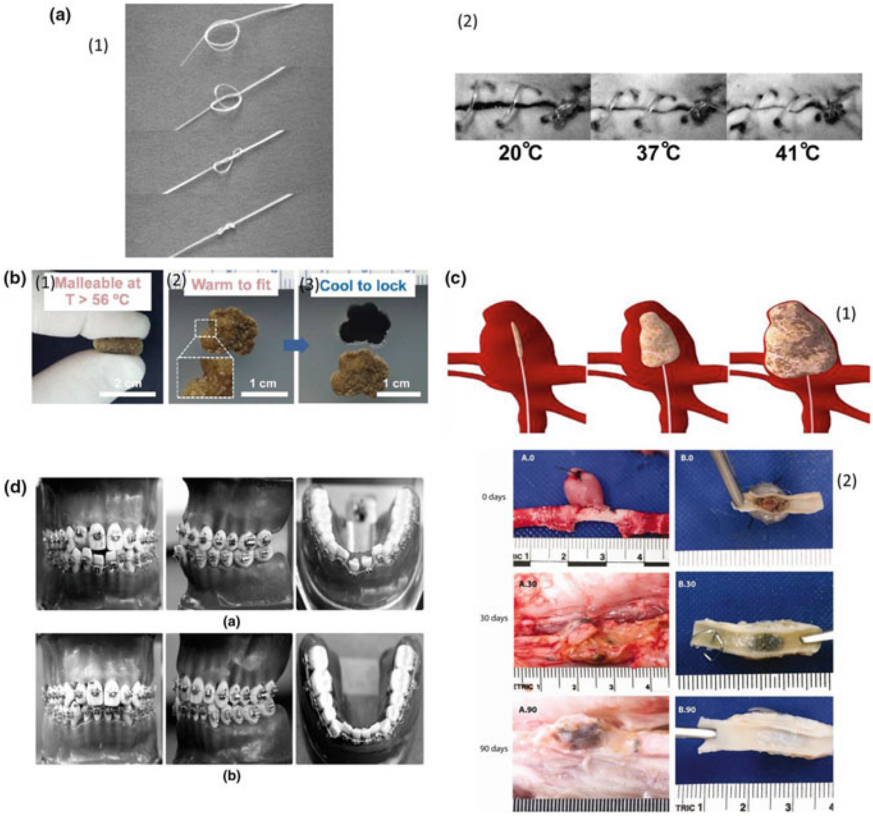

Fig. 9 Uses of medical devices based on SMP include: **a** tightening the biodegradable suture at 40C; **b** the malleability of self-fitting foam at its Ttrans; **c** the fitting of the foam into the irregular defect model; **d** the removal of the foam from the defect area after cooling; and **e** SMP foam before and after exposure to air [50]

3 Applications of Additive Manufacturing in Sports Industry

The first company to apply AM technologies to sports was Nike. Nike was able to decrease the sampling process from weeks to days by prototyping 30 alternative plate variations for its Zoom Superfly Fly knit. By utilising AM to create a running shoe midsole, Adidas was able to reduce weight and increase durability without compromising stability. Adidas intends to make custom shoes quickly and in-store using digital foot measurements and foot scanning technologies to deliver the most personalised shopping experience possible. In order to create a 3D model of a running shoe, New Balance works with athletes to gather mechanical data [51]. AM is used to make a biathlon rifle support. In order to create a rifle support that would fit the athlete's body and allow for a steady firing action, a 3D scan of the athlete's body was performed. Then, in order to reduce component weight while also providing structural protection and stiffness, topology optimization was paired with a FE review. It was discovered that the printed rifle support could sustain a force of 13.92 KN, or 14,294 times its weight (99.4 g). This outcome shows a 40% improvement over the original design, proving the viability of the suggested topology optimization plan. The printable rifle support can be utilised in biathlon because it weighs less than 100 g [52].

Using the fused filament fabrication (FFF) process, Aferdita et al. created a novel, precise approach for incorporating shock sensors in the interior of sports helmets [53]. Figure 10 demonstrates FFF printed PLA and TPU blocks with silica-coated fibres implanted in them. The use of FFF to incorporate Fiber Bragg grating sensors (FBGs) inside intricate polymer constructions, such as padding components for American football helmets, was reported and validated. Additionally, the possibility for embedding FBGs with FFF was validated, and a novel technique was presented employing stereolithography equipment (SLA). SLA produces prints of higher quality than FFF, however it cannot be used to embed polyimide fibres because of how they react chemically with the SLA resin. Depending on the application use-case, the higher quality prints produced by SLA must be weighed against SLA's greater cost and longer print time.

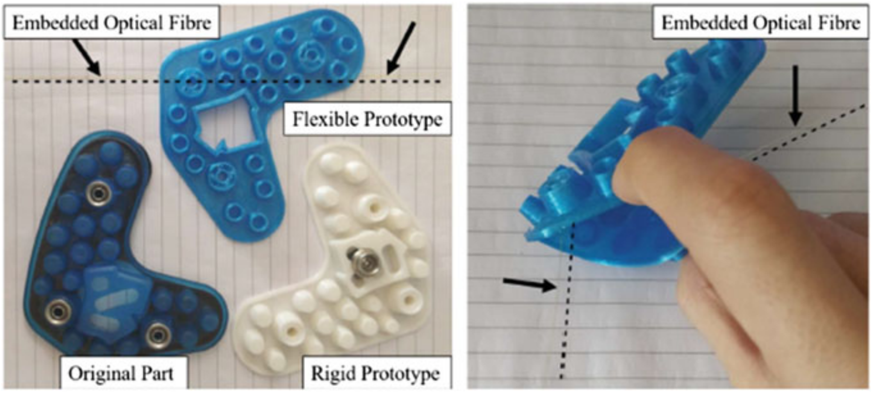

Fig. 10 Flexible TPU and rigid PLA sections with optical fibre implanted in them are modelled after the padding of a helmet. Without suffering damage or slippage, the fibre can flex and bend with the material

4 Customizing Surfboard and Stand-Up Paddle Board Fins Using a Parametric Method for Additive Manufacturing

Fins for stand-up paddle (SUP) and surfboards are made using 3D printing [54]. Figure 11 depicts the 3D printing of two fin designs, one of which was created using SLS and the other using a desktop FFF machine (Wanhao Duplicator i3, Acrylonitrile Butadiene Styrene material). The fins were affixed on a 2016 G-Whiz 9′4″ SUP board from Slingshot Sports. Ocean paddling on flat water was successful with both fins.

In order to build the cam systems for a compound bow, Serena Graziosi and colleagues considered the functional, manufacturing, and assembly limitations as well as the techniques used to assure the object's printability. The manufacturing method used the selective laser melting technology. The absence of integrated design techniques and the sizeable number of factors that need to be taken into account when making design decisions were recognised as the challenges faced by practitioners while designing for additive manufacturing. Figure 12a shows the redesigned geometry with the supports highlighted in red, and Fig. 12b displays the printed result as it was designed to be. Supports were needed to disperse heat, enabling a straightforward separation of the item from the platform, and support overhanging surfaces that were below the 45° limit. About half of the initial value will need to be sustained in terms of surfaces (Fig. 12a). Last but not least, Fig. 12c displays the sandblasted and support-free printed item [55].

Particularly in the field of athletics, orofacial injuries are a frequent cause of impairment. The main contributing factors to this injury occurrence are physical contact and a lack of protection. The hard and soft tissues of the mouth are protected by polymeric mouth protectors, commonly referred to as mouthguards, which are devices designed to be worn in the athlete's mouth while engaging in physical activity. A range of steps are involved in this paper manufacturing technique for creating personalised mouthguards, including preparing the mouth prototype, manipulating

Fig. 11 Comparison of the 2016 G-Whiz Slingshot SUP's original centre fin with versions made similarly using desktop FFF (second), and selective laser sintering (third) (3rd). One of the fins installed on the SUP board is shown in the right image [54]

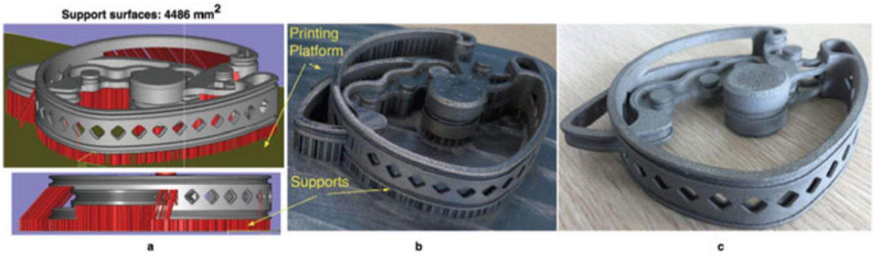

Fig. 12 **a** A summary of the supports required to ensure the object may be printed (in red); **b** the printed cam; and **c** the new cam following support removal and sandblasting [55]

the chosen thermoplastic sheet, and the final forming process as show in Fig. 13. A PEEK-based mouthguard might be designed using digital software, according to a study by Li and colleagues [56]. The finished produced devices and other guards made using conventional techniques showed no discernible differences in retention (vacuum-pressure forming). The dental design of 3-D printed mouthguards has to be improved in order to maximise impact attenuation. According to a separate study that used digital technology to build a high-elastic silicone rubber mouthguard, this strategy can help to enhance fit accuracy [57].

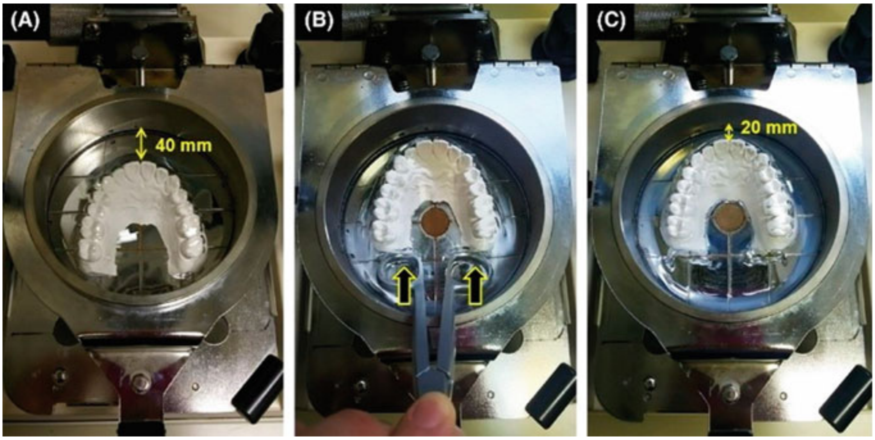

Fig. 13 Pressure equipment and moulding circumstances (condition MP) [58]

5 Challenges in Production for Biomedical and Sports Industry Using Additive Manufacturing

- Given the lack of longitudinal evaluations and small sample numbers in the majority of research, the long-term durability of AM materials for sporting applications is unknown.
- Compared to conventional production methods, additive manufacturing is often slower.
- Postprocessing might take a lot of time and effort.
- Many AM-produced pieces still need to work with traditional parts to complete products, which restricts geometry.
- Manual involvement and an understanding of design for are still needed when using optimization software.
- New items created with AM might not adhere to athletic laws.
- The results of laboratory testing might not apply to real-world situations.

6 Conclusion

Particularly in the medical industry, additive manufacturing is a powerful, innovative, ground breaking, and quickly expanding technology. Patient-specific surgical models, surgical equipment, and personalised prostheses are the four main fundamental applications of additive manufacturing (AM) in the medical industry that are linked to recent advances. AM has recently offered a variety of applications in medicine, including prosthetic dentistry, the creation of various surgical cutting and drilling instruments, and the use of craniofacial implants for hip, knee, and spinal implants.

Due to its outstanding manufacturing methodology, additive manufacturing (AM) has significantly increased growth in the biomedical and sports industries. It has completely changed the tested testing procedures and methods. The biomedical industry can now approach implants in a different way because some places were beyond the capabilities of conventional production techniques. However, with additive manufacturing, more complicated implant designs like cranial plates, stem implants, and knee joint implants may be quickly created. Since these implants are individually-specific and cannot be produced similarly for every patient, patient specification is strongly advised. Similar to other industries, the sport industry has profited from additive manufacturing in terms of lightweight, part customisation, and sophisticated design solutions. For a spacecraft or communication satellite, reducing weight is frequently a top concern because it increases system effectiveness and uses less fuel.

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Chapter 14
Additive Manufacturing: Environmental Impact, and Future Perspective

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Abstract Additive manufacturing (AM) are the latest fabrication techniques that has generated interest worldwide. As it allows to design any solid 3D object to be printed using computer-aided design (CAD) and analyzed using CAD. For complex geometries and material combinations, CAD is often further facilitated with high-productivity computing resources. This combination of hardware and software facilitates the manufacturing process to produce anything imaginable. In contrast to subtractive/conventional manufacturing, which creates an object by removing material, additive manufacturing (AM) uses the technique of combining materials, typically layer by layer. While rapid prototyping and end-use product manufacturing are the next steps for additive manufacturing applications, the effects of these manufacturing processes and associated material flows on the environment are yet to be discovered. Along with the energy and resource usage of the AM unit, it's important to consider the effects of producing (powder) materials and finishing parts. From the environmental point of view, it is obvious that the additional effects produced during production should be offset by functional upgrades during the part's use phase. The continuous growth of the various technologies of AM is an eye-opener for different fields. The technological advancements in AM can be a game changer in many areas like automobile, construction, medical, toy, and also in defense applications. This chapter provides details of the consequences of AM on the environmental and also provides the future prospectives in various industrial sectors.

Keywords Additive manufacturing · 3D-Printing · Environmental impact · Future prospectives · Life-cycle assessment · Waste management

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1 Introduction

Additive manufacturing technology (AM) has revolutionized the way products are designed, developed, and manufactured in the twenty-first century. The technology has enabled manufacturers to fabricate complex structures and parts with a high degree of precision, accuracy, and efficiency. While AM has many advantages for industry, it also has a number of implications for the environment. In this chapter, we will discuss the environmental impact of AM, analyze the environmental benefits of the technology, and consider ways to minimize it.

AM is built through layer by layer using 3D printing, a process that has gained popularity due to its ability to produce complex parts rapidly with minimal waste. Although this technology has the potential to reduce waste by 30–60%, increase efficiency, and provide greater design flexibility, it also comes with a number of potential environmental impacts. For instance, the use of certain materials, such as plastics/polymeric, and ultra-fine powders, may have a both positive as well as negative impact on the environment.

Additive Manufacturing (AM) technology has been found to have substantial environmental benefits over traditional manufacturing technologies. AM technology can reduce energy consumption, water use, and the amount of material waste that is associated with the production of components, tools, and consumer goods. Furthermore, AM technology can reduce the number of hazardous materials that are used in the production of components and consumer goods. Additionally, AM technology can reduce transportation costs, as components can be produced closer to the point of use.

Additive Manufacturing (AM) technology can emerge as a cost-effective and efficient means of producing parts and components for a wide range of industries. However, this technology is not without its environmental impacts.

In recent years, the environmental impact of additive manufacturing (AM) technology has emerged as a critical issue. The capacity to reduce waste, operate with fewer raw materials, and assess the environmental impacts of production using 3D printing has caused increased interest in AM among manufacturers who are looking for more sustainable and efficient processes. This chapter focuses on resources and their consumption and waste management, pollution and life cycle assessment, and the future prospects of additive manufacturing and its application in different fields.

2 AM Industry Resource Consumption

In additive manufacturing resource consumption can be categorized in two i.e., (1) Direct and (2) Indirect resource consumption, and the degree of its consumption may vary with respect to the additive manufacturing technique and the industry (eg. DED, PBF, SLM, SLS, Plasma arc and gas metal arc, stereo-lithography, binder jetting), The Direct resource consumption is (1) power/energy (laser, electric arc, electron beam, ultrasonic vibration) (2) material/Feed (metal powder, filler wire, sheet, polymer filament). (3) Shielding gas (Helium, Argon, Nitrogen) which is used to protect the molten structure to avoid metallurgical defects such as porosity and hydrogen cracking in the printed structure is considered a direct resource. While the coolant (water, lubricant) and support structure are considered as the indirect resource.

Most of the AM-produced parts require post-processing to some degree i.e., either heat treatment or machining process these can be considered as indirect resources as it depends on the type of quality metallurgical properties and the finishing required. Even though additive manufacturing is considered as 97% material efficient theoretically, in practice energy consumption is comparatively high as it produces design-specific and low-volume products. It has been observed that, data related to energy consumption is varying with respect to the geometrical dimension of the build part, machine, processing parameters, and material. However, the energy consumption is far lower than compared to conventional processes and it reduces the material waste.

2.1 Waste Management

The additive manufacturing process produces a lesser amount of waste compared to subtractive manufacturing techniques, and it can reduce up to 90%. However, this doesn't imply that AM doesn't create waste, but it may occur due to human and machine errors. Metal AM parts often require post-processing before they can be used in the market, which can include machining to improve aesthetics, reduce friction, and remove imperfections. However, the environmental impacts of these steps are often overlooked.

Post-processing can affect the performance and appearance of AM parts due to factors such as porosity, surface roughness, anisotropy, residual stress, and complex geometries. Parts produced through conventional manufacturing have high static and dynamic strength than those produced without post-processing. While the parts AM produced through EBM parts have minimal residual stresses, which is an advantage over SLM and DED, but often require more post-processing due to their rougher surface finish. To accurately measure the environmental impacts of metal AM, standardized methods should take post-processing into account.

In the case of wire-based additive manufacturing the rate of depositions is higher than compared to powder bed fusion. Typically, it requires to have large machining allowances to achieve desired design and shape. the cost per kilogram saved is offset by a wasteful material loss from the machining process. Additionally, the residual material from partially used spools may not be suitable for reuse, unlike the ability to reuse and recycle un-melted PBF process powder. It has been suggested that waste generated by laser sintering powders (polyamide) can be used as filaments for the FDM process. In the case of SLM, PBF generates waste through support structures for overhanging which are often removed and are non-usable. Researchers need to focus on reducing on use of support structures. In the case of PDF, EBM powders can be recycled but up to a certain limit, as it modifies the powder characteristics i.e., compositional change and property deterioration. Feeding of multiple powders to build a desired product but these mixed powders become unusable because of the mixture of multiple powders. AM technologies use a wide range of powder to fabricate solid objects, but data is missing to show the total amount of waste generated. During the process, semi-fused powders and support structures are created for overhanging parts can also be considered as waste as they are unusable for further processing.

The FDM market has seen a rise in development, leading to the manufacture of various filaments to improve performance. However, this has caused environmental concerns due to plastic waste. To address this, biodegradable or biocompatible filaments are being developed, but they are not as strong or resistant to moisture as traditional filaments. Limited research has been done to optimize FDM printing paths, and support structures for material reduction, and few efforts have been made to evaluate metal and ceramic scrap for this process. The current AM industry has a small share of the market, which may be why no action has been taken to investigate waste management and promote sustainable manufacturing.

2.2 Pollution Control

Additive Manufacturing (AM) is a rapidly growing technology that has the potential to revolutionize the way products are designed and manufactured. However, with the increased use of AM, there is a need to understand the potential environmental impacts associated with this technology. One of the most important environmental concerns associated with AM is the potential for pollution. Pollution can come in many forms, including gas, liquid, solid, and sound. The toxicity of these effects on the environment is rarely studied.

Gas pollution is a major concern with AM, as the process involves the use of various compositions of Filaments such as., Acrylonitrile butadiene styrene (ABS), Acrylonitrile butadiene styrene + 0–3% polycarbonate Acrylonitrile styrene acrylate, High impact polystyrene, Polyethylene terephthalate glycol, 80% PETG + 8–12% fiberglass filings, 30–35% polycarbonate + 55–65% ABS, PETG + carbon-based conductive additives, melting of these tend to release volatile organic compounds (VOCs) into the atmosphere. From the available literature, it was observed that there is a large variation in volatile organic compounds and it is significant to mention that ABS filaments are expected to pollute more than compare to other filaments.

As these VOCs react with the atmosphere can have a negative impact on air quality and can contribute to skin irritation, and cardiovascular problems if exposed for longer periods of time and temperatures. It is suggested to use 3D printers in fully vented rooms to avoid problems associated with it. However, studies also suggest that the threshold limit is lower of when compared to the conventional manufacturing process. The process needs to be optimized in these areas for a better understanding of the results. Only a few countries in the globe have proper legislation on tolerance threshold limit is defined regarding VOCs.

Liquid pollution is also a concern with AM, as the process involves the use of various liquids, such as coolants and lubricants, to create the desired product. These liquids can be released into the environment, leading to water pollution. Additionally, the use of certain materials, such as metals, can lead to the release of heavy metals into the environment. Heavy metals can have a negative impact on water quality and can lead to the contamination of drinking water sources.

Ultra-Fine dust pollution is also a concern with AM, as the process involves the use of various solids, such as powders, and resins, are used to create the desired product. These solids can be released into the environment, leading to land pollution. Additionally, the use of certain materials, such as plastics, can lead to the release of microplastics into the environment. Microplastics can have a negative impact on land quality and can lead to the contamination of soil and other land resources.

Given the potential for pollution associated with AM, it is important to conduct studies on particulate matter formation during printing and the explosive hazard of material powders during handling and use. These studies can help to identify potential sources of pollution and can provide valuable information on how to reduce or eliminate these sources. Additionally, these studies can help to identify potential safety hazards associated with AM and can provide valuable information on how to reduce or eliminate these hazards.

The AM process reduces the consumption of raw material when compared to traditional manufacturing techniques and moreover, it reduces the different cycles of manufacturing steps which in turn reduces the pollution and waste into the atmosphere i.e., improved carbon footprint.

2.3 Safety and Health Hazards

It is important for the operator to take precautions when handling raw materials (powders), and feedstock, and operating the printing machines. As the use of ultra-fine powders in the AM process it can be a potential source of fire or explosion. In addition, ultra-fine powders tend to agglomerate easily, and oxidation. Dust may accumulate in the feedstock; this includes regularly cleaning and maintenance of machines and the use of appropriate dust collection systems.

The most hazardous substance is the condensate that results from this process is the evaporation and expulsion of liquid metal, which makes filter replacement, as it is considered as the most dangerous part of the printing operation/step. The use of high-power-density heat sources can result in the formation of spatters, which can deposit fine metal particles within the chamber.

These heat sources, such as the laser, electron beam, or electric arc, can be dangerous due to their high energy density. Operators should take the necessary safety precautions. This includes wearing eye protection when working with lasers and other high-power-density heat sources, as well as wearing a respirator when handling ultrafine alloy powder feedstock used in Direct Energy Deposition (DED) processes. This is because these powders can be hazardous to the eyes and respiratory system, potentially leading to diseases such as asthma. The health risks are similar to those associated with welding, and operators should be aware of the potential dangers.

In addition to the potential health risks posed by powders, fumes, and volatile Particulate matter can also be hazardous. Fumes are a mixture of gases and particles that are released during the AM process. These fumes can contain a variety of metals, that are hazardous. Inhaling these fumes can cause a variety of health issues, including immune system dysfunction and upper and lower respiratory tract infections. It is important for an operator to wear protective clothing and respirators, as well as ensure that the work area is well-ventilated. Additionally, it is important to ensure that all AM equipment is properly maintained, and follow all the safety protocols are followed. By taking these precautions, workers can reduce their risk of exposure to hazardous substances and protect their health.

2.4 Life Cycle Assessment of AM Process

The eco-efficiency of actual production processes is a major area of research in engineering, and it is important to consider the environmental impacts of production equipment, technical building services, and energy supply. Life Cycle Assessment (LCA) is an established method used in sustainability management to calculate the environmental impacts from all life cycle stages of a product or system. This section will explore the benefits, impacts, and challenges of life cycle assessment in manufacturing processes. Specifically, it will discuss the benefits of life cycle assessment, the impact of life cycle assessment on additive manufacturing efficiency, and examine the challenges of implementing life cycle assessment in manufacturing processes.

This tool is used to evaluate the environmental impact of a product or process throughout its life cycle, from raw material procurement to end-of-life management. However, this is difficult to scale the complete life cycle assessment of the additive manufacturing process, as it requires a wide range of data in order to evaluate. Knowledge of materials, mechanics, physics, and chemistry, and technologies in information, manufacturing, mechanical, and energy engineering is required, this tool can be used to identify areas in a manufacturing process that are most environmentally damaging, enabling manufacturers to make changes to reduce their environmental footprint. The LCA can be used to determine the most cost-effective and sustainable solutions for manufacturers, as well as how it can be used to meet corporate social responsibility goals.

LCA is an effective way to understand the environmental and economic impacts of the product life cycle. It was observed that energy consumption is reduced in AM process, and this particular technique removed the cost of inventory and reduced the usage of raw materials by creating customized products with high design accuracy. When compared to traditional processes AM majorly cut down the transportation cost as it can be printed onsite and delivery the item to the customer. efficiency and the results indicated that LCA can lead to considerable cost savings and environmental benefits. The research found that data on LCA of AM is marginally low, to provide both quantitative and qualitative data to help companies assess their production processes and identify areas for improvement. Additionally, the findings showed that LCA can enable companies to optimize their operations, reduce their environmental footprint, and create more sustainable production methods. By incorporating LCA into their manufacturing processes, companies can gain greater insight into their operations and become more efficient and environmentally friendly.

It has been identified three primary considerations for minimizing the environmental impact of AM. First, they suggest that the use of recycled materials should be maximized. By doing so, the consumption of resources is minimized, thereby reducing the amount of waste generated. Second, they recommend that energy efficiency should be taken into consideration when selecting materials and processes for AM. The use of energy-efficient processes and materials can significantly reduce the carbon footprint of AM. Finally, they propose that the use of environmentally friendly materials should be prioritized. By utilizing materials that have a lower environmental impact, the amount of waste produced by AM processes can be minimized. Taking these considerations into account can help to ensure that AM processes are as eco-friendly as possible.

3 Traditional Supply Chain and the Competitive Dynamics of Economies of Scale

For years, traditional manufacturing techniques have relied on a design-build delivery model. In the market, the roles and responsibilities among the various participants are clear. Designers translate customer needs into viable products. Producers, on the other hand, have facilities that emphasize on efficiency and low-cost production. Over the past four decades, these producers have increasingly relied on distributed and extended supply chains, scouring the globe for the lowest-cost suppliers to manufacture components and sub-assemblies. The production methods employed by the manufacturers are mostly subtractive manufacturing methods that start with a solid physical form followed by grind, cut, drill, mill, lathe, and other material removal processes to manufacture and build desired components, sub-assemblies, and final finished products.

In this model, minimizing variations to enable the repetitive production of interchangeable parts provides a competitive advantage. In the 1990s, companies were built on this model by pursuing design for manufacturing (DFM) strategies (see for example, Ulrich and Eppinger 1995; Boothroyd et al. 2002), emphasizing on designing parts that could be built cost-effectively using traditional manufacturing processes. This model, which changed the object of design from creative expression to cost-effective production and assembly, required simplified designs developed according to a series of design rules that favored reproducible parts optimized for high-volume manufacturing and material-handling methods. Several generations of designers and engineers have been schooled in this approach; many now view design as a creative process of circumnavigating the constraints imposed by traditional manufacturing processes.

3.1 Future Prospectives of Additive Manufacturing

Additive manufacturing is a manufacturing method which proceeds through layer by layer. The source of the manufacturing method could be either Computer Aided Manufacturing (CAM), Electron beam, Laser beam, Computer Numerical Control (CNC), Computer-Aided Design (CAD) or Laser Scanning [1]. Although the maturity of the techniques was in the late 1980s, the technologies have emerged as promising in the last decade only. The evolution of the AM and the timelines of the industrial revolution is depicted in Fig. 1 [1].

In AM process involves continues supplying of heat on build-layers resulting in high residual stresses which affect the quality of microstructure, and lead to directional mechanical properties. Macro defects such as porosity and areas of un-melted powder, are distinctive characteristics of AM technologies. In addition to these defects, unwanted phases can emerge during AM, which altogether can have a detrimental effect on mechanical properties. As a result, this microstructure control becomes a primary challenge in AM, particularly in complex alloy systems. To avoid

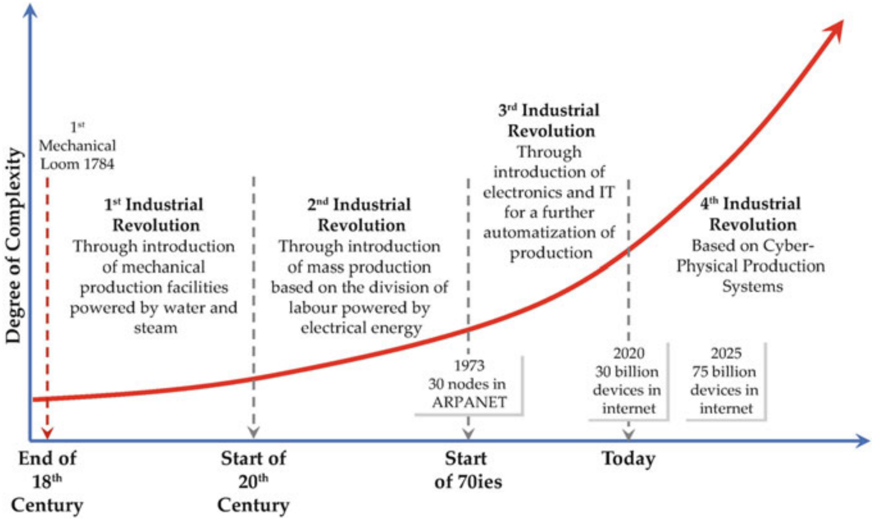

Fig. 1 Evolution of additive manufacturing: the timelines of industrial revolution [1]

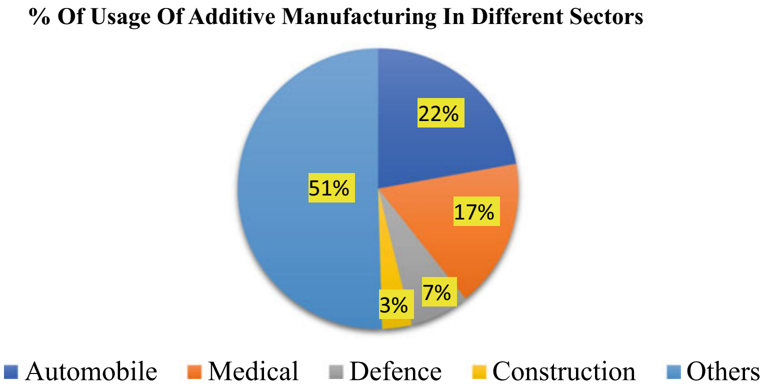

Fig. 2 Applications of the AM in various sectors [4]

these aforementioned problems researchers have to optimize the process parameters to design and build the customized product.

The emerging AM techniques have potential applications in various sectors. For e.g: 17% of Medical tools are designed and manufactured by AM, Construction companies have initiated to use of AM as a tool and it occupies around 3%, While Engineering components such as automobile, Space, and defense industries consume AM-built products i.e., about 70% of the total market share. Moreover, these AM techniques require extensive research and development to resolve challenges in material selection, built speed, Processing parameters, high initial cost, and non-linear behavior in the design of the additive manufacturing systems. Sector-wise applications data of AM is shown in Fig. 2.

3.1.1 Aerospace Sector

AM registered an annual growth rate of more than 30% in the present decade in the aerospace sector. Showcasing the fastest growth of the technology it is obvious to have limitations in many parameters for the manufacturing of the component. AM has reported an increase from 8 to 10% recently by application. AM Gradient materials or design being a solution to solve the challenges of the aerospace industry [6]. Materials having various properties can be chosen as per the design requirement could be one of the options to resolve various issues in the aerospace design. By selecting processing parameters judiciously, ceramic materials with different dielectric, magnetic, or electrical properties could be created as a graded structure. The creation of novel functional geometries, such as biomaterial flexures or constructions with rigid surfaces and a ductile core, that are expensive or difficult to fabricate otherwise is another application [5]. 3D printing has opened doors for multi-material design and potential applications in the Boeing Airbus [6]. Many 3D printing techniques can be modified to 4D techniques but with few challenges. Another area of perspective in AM technologies is 4D printing where the fourth dimension, describes how geometry changes over time as a result of active functionalities [5]. The use of AM in the aircraft industry leads to reducing inventory levels as well as the costs of logistics. The major future impact of 4D printing will be in military and defense, automotive, clothing, healthcare, construction, and aerospace [6]. Often used forms of 4D printing constitutes, Polyjet and syringe printing. In order to give assurance for numerous quality issues in the aerospace sectors, smart material (like Shape Memory Alloys (SMA) and Shape Memory Polymers (SMP)) development processes must be urgently established and integrated into aerospace applications. For large-scale components especially made of Inconel alloys, hybrid printing could be an option [2]. Incorporation of techniques like Selective Laser Melting (SLM) and DED also known as Laser Metal Deposition (LMD) is crucial as it facilitates the production of sufficiently larger parts with complex geometries. Combining the benefits of both AM technologies to create complex structures would be of great interest. This can be beneficial in the production of large components with precise geometries and good mechanical properties. For the hybrid part to be strong, there must be strong bonding between the pieces. Additionally, proper DED process execution and post-solution annealing customization to the DED microstructure, notably the dissolution of the complex phases in the Inconel structures, are essential.

Laser Metal Deposition (LMD) is one of the AM processes that qualify for relatively greater build rates, which can speed up the process and cut downtime, making it possible to manufacture large components. Materials that can be worked with LMD include titanium alloys, alloys based on nickel and cobalt, carbides, stainless steel, and nickel-based alloys [7]. Other possible future prospectives include design Verification of an Airline Electrical Generator, Engine Components for a Fanjet Engine, Prototyping Air Inlet Housing for Gas Turbine Engine Fabrication of Flight Certified Production Castings [8]. Apart from the new technologies, proper material selection for the end product is another major concern. In the case of aerospace components, properties such as surface roughness and fatigue behaviour of the materials working in extreme environments would be more of more focus [9].

3.1.2 Medical Sector

A few very important and future prospective applications in the medical sector are the world's first Jawbone transplantation, the Manufacturing of prosthetics sockets, tissue regeneration, artificial blood vessel, and many more [9]. During the manufacturing of medical implants by AM, well-recognized standards need to be maintained. But some of these implants made by AM don't follow these standards and may lead to failure [10]. The shape recovery hydrogels made out of 3D printing are one of the main applications in the pharmaceutical industry [11].

The most widely used 3D printing technologies in pharmaceutics and drug delivery are FDM and inkjet printing. Despite the fact that these technologies offer fast drug release, patient-customized pharmaceuticals, and large dosage loading of drugs, they are comparatively less productive than conventional techniques. Furthermore, only a few technologies, including direct ink writing for intravenous drug delivery systems, are used for 4D printing in the pharmaceutical business [11].

Titanium and its alloys have attracted a lot of attention for biomedical applications due to their superior mechanical characteristics and biocompatibility such as orthopedic implants. Their construction, structural design, and composition can be further customized to enhance critical features like composition, structural design, and fabrication. Further tailoring can be imposed to improve key properties which allows them to become more compatible with the human body and lowering their cost. Fabrication of titanium-based composites is still a challenging task. So, new technologies need to be developed for producing low-cost porous titanium matrix composites for various medical applications. Apart from the bio- implants, AM can be used for bone regeneration [12]. The ability of these AM techniques could rise till the numerical model design of the choice material has the capabilities of tailoring the properties and robocasting the structure mainly the architecture which can be controlled as per the specifications. Heat treatment-free materials can be developed for the best use of the technology in driving the new materials input in the human body. More accurate result-oriented technology ensuring best-in-class medical solutions could be possible in the coming days. intensive, and expensive process. AM technology also supports the automated, fast, and inexpensive development of microfluidic devices, with a more regenerative and repetitive way of approach. These fluids are potentially biocompatible and transparent materials that allow both unhindered cell culture and imaging [12]. Despite of extensive research on topological optimization based on continuum models, the topological design of lattice structures that can be easily produced by AM which can exhibit anisotropic mechanical properties similar to human bones.

3.1.3 Defence Sector

According to aerodynamic theory, an elliptical wing with an elliptical span-wise lift distribution has the lowest induced drag. This shape, however, is difficult to manufacture using traditional techniques but can be easily printed using AM techniques. Additive manufacturing technologies have found applications in the defense industry, where they are used to create lightweight parts with geometric and material complexities. To fully utilize the advantages of this technique, Electron Beam (EBM) is used to manufacture complex aerospace components such as the Ti-6Al-4V Bleed Air Leak Detect bracket [13–15]. High-performance polymers and their composites for powder-based AM to create strong, lightweight parts with intricate geometries to meet demanding specifications in automotive, aerospace, and military applications Printable composites have multiple capabilities, including mechanical, thermal, and electrical properties, thanks to the reinforcements they contain [16]. Advanced Composite Structures (ACS), a US-based company, manufactured a camera fairing that is used by military aircraft in forward-looking infrared cameras.

Hindustan Aviation Limited employed 3D printing technology to create a prototype model for a 25-kN aviation engine [17].

3.1.4 Automobile Sector

Building prototypes, jigs, and fixtures, tooling, low volume end-user goods and concept models, as well as reproducing parts, are all examples of 3D printing's uses in the automobile sector. Innovations made possible by 3D printing include variable turbo technology for Koenigsegg. Safe, intelligent, and environmentally friendly LM3D 3D printed car series from local motors, on-demand 3D printing of Audi replacement parts, new Blade supercar chassis construction by Divergent Microfactories, race-ready Williams-F1 parts, thumb tool for BMW, etc. [14]. Apart from these the various AM technologies can showcase more in development of automobile sectors [19]. Recent innovations in AM show that researchers have started exploring the design of compositions concept of material to build AM products that can have promising metallurgical and mechanical properties than the traditional counterparts.

3.1.5 Other Sectors

Decentralization may be made possible in the future by dispersing the workload among factories and equipment with the help of efficient cloud service use [18]. Another future area for AM is the sustainability issue. By utilizing just-in-time production, AM may significantly contribute to decreasing waste resources and lowering energy use. Furthermore, it is possible that 3D printing and digital manufacturing will have an impact on society. The first step is to redefine the function of the employee in the industry so that they work on management, design, and analysis tasks rather than serving as the labor force. Second, user participation in the design and manufacturing phases is facilitated through platforms like the maker movement and do-it-yourself.

For instance, by converting the classroom into a miniature hands-on factory, students/researchers can create their own products. Processing functionally/structurally-graded components utilizing either bimetals or metal-ceramic composite combinations is a developing topic that is receiving more attention in regard to future growth. By altering the composition and structure of a component inside a single part, these structures combine the finest qualities of many materials. They occasionally use different metals or ceramics for site-specific features. DED is the predominant technology for their construction due to the multi-material makeup of these structures [20]. Despite the growing prospectives for alloy design utilizing LAM in the field of materials engineering, there are still issues that must be resolved to attain full utilization. For some applications, these difficulties are primarily technical in nature and depend on factors like the high cooling rate of additive manufacturing (AM) and material compatibility, both of which pose serious difficulties for the processing dependability of some of the main metallic materials used in AM. However, in other application areas that have not yet caught up with the demand for alloy design in AM, the availability of material in the form of powder or wire feedstock can cause problems in the process chain. These issues are finally resolved by the venerable issues of property confidence and dependability, which can only be resolved through rigorous testing and characterization. More extensive research is also going on in biodegradable materials [21], nanomaterials [22], advanced material data analysis and approaches [23], future foundation building.

4 Conclusion

1. AM has revolutionized the manufacturing industry by enabling the production of complex structures with precision and efficiency.
2. AM presents numerous advantages, but it is important to consider its environmental implications. These include resource consumption, waste generation, and pollution.
3. AM technology has the potential to reduce energy consumption, water use, and material waste compared to traditional manufacturing methods. It can also decrease the use of hazardous materials and lower transportation costs through localized production.
4. Effective waste management strategies are essential to minimize the environmental impact of AM. Post-processing, proper disposal of unused materials, and recycling efforts should be considered to reduce waste generation.
5. Pollution control is another important aspect to address. Measures should be taken to mitigate gas, liquid, and solid pollution associated with AM, including the release of volatile organic compounds, heavy metals, and microplastics into the environment.
6. In conclusion, while AM offers significant benefits for the manufacturing industry, it is crucial to adopt sustainable practices and minimize its environmental impact. By addressing resource consumption, waste management, and pollution control, we can ensure that AM technology is used responsibly and contributes to a more sustainable future.

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Chapter 15
The Economic Impact of Additive Manufacturing Industries

Krutika L. Routray and Sunirmal Saha

Abstract Additive manufacturing, colloquially referred as 3D printing, is currently considered as an approaching mainstream adoption for highly flexible processing technology to be implemented by manufacturing industries. Moreover, additive manufacturing technology can be applied to design customized products without cost penalty and applied on any kind of plastic, metal, ceramic, concrete materials. Additionally, additive manufacturing facilitates the manufacture of complex and integrated functional designs in a single step, thereby potentially reducing the need of molds, shapes, and assembly work. Our findings show the five key principles relevant to manufacturing industries contributing to the economies of scale on incorporating to additive manufacturing technology. Furthermore, we have analyzed that once additive manufacturing technology is utilized at full capacity, no implications on increased volume on unit cost is found. In so doing, we have provided implications of additive manufacturing technology on profitable basis which provides motivation for future research. Meanwhile, it is seen that there is a demand for additive manufacturing in competitive markets as it reduces the barriers to market entry and paves a way to provide multiple markets at a single time. This ultimately result in lowering prices for the demand of consumers.

Keywords Additive manufacturing · Manufacturing industries · Flexible manufacturing · Integrated functional designs · Economic modeling

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1 Introduction

Additive manufacturing (AM), commonly recognized as 3-D printing, encompasses manufacturing a material by depositing material layer-by-layer approach based on a computer-controlled fabrication process [1–3]. Additionally, AM allows the manufacture of complex and integrated functional designs through a single step process which potentially reduces the need for assembly work [4, 5]. It is anticipated to reconsider design, digitalize industrial manufacturing, claim to meet the demands, and modify the material or the desired products for least cost [3, 6]. Various strategies and agendas are being used by the state economic development programs regarding the performance of their manufacturing industries [7]. To date, most manufacturing industries have adopted the use of additive AM technology since 1980s when it was initially used for prototyping applications only [2, 8–10]. While it is not economical for AM technology as a feasible approach to manufacture materials for all available applications still, it has gained demand amongst manufacturing industries which provide high value and customized products at low values to obtain substantial benefits such as aerospace and medical industries [5, 11–15].

Innovators have demonstrated potential benefits of AMs for firms in various manufacturing markets. For example, in the shoe industry, manufacturers have adapted AM technology since years to test new designs at a speeder rate and quicken the designing process [16, 17]. Not only complex geometrical designs but also manufacturing industries based on customizable material properties have also adapted AM such as Nike in 2013 offered a customizable football cleat produced via. AM [18]. Simultaneously, AM also offers an ideal alternative to industries by enabling them to streamline market entry into a relatively mature industry [2, 4]. For example, currently, the AM technology is being used to create hip and knee joint replacements, cranial reconstruction implants and spinal implants. As of 2019, over 600,000 implants are estimated to be produced with the help of 3D printing. By 2027, this number is set to top 4 million. Further industrial applications of AM are common in aerospace industries, defense, medical markets, automotive and machinery components [19–22]. The prime advantage for manufacturing industries to include AM technology in the manufacturing process is that it enables the flexible production of complex geometrical designs with customized products without cost penalties [23–27]. For designing physical models' layer-by-layer, various AM approaches can shape complex geometries with less cost penalty viz. machining, molding, casting, and specially made tooling [28–30]. Consequently, AM includes several methods such as material selection, printing accuracy, speed, price of equipment, and finishing quality amongst others which has created spark in a new industrial revolution, hence reducing the need for assembly activities. Thus, AM technology significantly affects the costs of flexibility, individualization, capital costs, and marginal production costs [23, 31, 32]. Majority of the manufacturing industries have adapted AM as a new generation of manufacturing but concurrently specified it as highly strategic regarding the economic scenario.

Firms provide information on opportunities and challenges about markets. This creates a probability to know the market conditions and create modernizations that can meet market demands and provide profit to the makers. Hence, AM technology directly affects the market structure by affecting a single firm's production processes. Innovators are continuously developing and sharing 3D models which are being developed for selling purposes in marketplaces [31–36]. Furthermore, innovators are even developing and providing their own 3D printers for home usage and industrial usage extending the scale and scope of manufacturing options. Gartner in 2014 rightly predicted that use of AM technology in industries will reach a level of mainstream adaptation between 2016 and 2020 and now-a-days the most important aspects of Industry 4.0 is 3D printing [37]. AM is now a leading technology in almost all industrial and manufacturing sector owing to the wide range of institutional push and possibilities offered due to 3D [4, 38]. According to reports, AM will impend the futuristic production systems, and manufacturing industries will control its potential to reach essential goals. AM now has been used in variety of industrial applications including aerospace and health care to consumer goods. Boeing has numerous hundred components on its 787 aircraft prototype and, also, customs some thermoplastic components produced with Selective Laser Sintering technology on commercial 737, 747 and 777 programs [23, 39–42]. In addition, industries have AM technology in in medical markets, defense, automotive and machinery components.

This chapter outlines the economic implications of AM on manufacturing markets. Despite the current research interest of AM technology, effects of AM technology on economy are still unusual. AM is considered to be gradual developing in niches with limited and small markets and more likely to be engaged in large scale industries in the upcoming years as it has demonstrated great flexibility in adapting to the requirements of different functions. This is possible as AM uses computerized manufacturing process which directly transforms 3D data into physical parts, without the help of any casts, shapes, or tools [43]. In addition, AM technology can produce functionally integrated parts in a single production step. This reduces the requirement of assembly activities thereby affecting individualization, the costs of flexibility, marginal production, and capital costs [25, 31]. AM is an emerging technology that reflects the nature and stage of maturity of the innovation system and has viability of high-end niche manufacturing industries in different directions, but this doesn't indicate that small markets can bring new technology to maturity and infiltrate the larger audio market sections. Hence, there is a need of economic assessment and evaluation of AM technology in manufacturing industries [44, 45]. Manufacturing industries willing to practice this emerging technology are not only engrossed on obtaining economic benefits but focused on competitive advantages to stand out in the market along with economic benefits. There are five key principles related to economic impacts of AM in manufacturing industries. The first key principles of AM are pertinent to manufacturing industries and their potential effects on an industries' payment role in a monopolistic setting. AM technology promotes autonomous interoperability, flexibility, efficiency, and cost reductions so the second key principle comprises of models on manufacturing sector that assess advancements in the interoperability and flexibility of manufacturing systems [10, 41, 46]. This includes all the dimensions of AM technology and its effect on competition at industry level. Thirdly, the economic impact of AM focuses on the future use of this technology in manufacturing industries and adopting it at firm level. Using AM technology will affect the opportunities, applications, and constraints. Hence lastly, this chapter focuses on the consequences of industrial practitioners for market structure at industry level.

2 Key Principles for Manufacturing Firms and AM

2.1 Technological Background

Owing to the demand for customization of complex designs and higher transportation costs for the delivering the final products, AM technology plays the vital role in manufacturing industries characterized by its flexibility and no cost penalty. AM enables product innovation as design iterations are low-cost and required parts can be produced rapidly. Also, AM technology is used to produce any part of physically feasible product design assembled in a 3D model, as products are manufactured layer by layer [2, 3, 47, 48]. This provides solution space for product designs, in essence solely limiting it to designers' creativity and physical laws. Theoretically, any physically feasible product design can be produced by using AM technology based on a 3D model [25, 49, 50]. Consequently, complex designed products designs can be modified according to their desired function rather than the constraints that has limited the performance of supply chain. Also, manufacturing industries can produce highly customized products owing to the preferences of the costumers. This in turn increases the costumer's readiness to pay for the product according to their demand, and the manufacturer charge the costumers a premium price instead. Now-a-days, various websites are intended in such a way that allows the costumers to design their personalized products by the help of 3D product configurator and after finalizing the product preview, AM technology can be used to produce the same desired product. This not only avoids the additional manufacturing cost but also produces a potentially strong product that meets the costumer's requirement as other technologies entail modular product architectures by recombining pre-assembled parts which produces different variants of a same product [51]. Hence AM is capable to resolve the scale scope dilemma of the manufacturing industries and supply the better product as other technologies involves multiple production steps and additional costs for inventories of semi-finished and finished goods. Manufacturing industries can obtain the profit by AM as the makers can tailor their products to meet the unique needs of the costumers without cost penalty [19, 40, 52, 53].

Though location decisions are made infrequently for most manufacturing industries, they can have a long-term impact on the market profitability and success from economic point of view. Considering the basic calculations, the actual fixed costs include overhead costs, the ongoing expenses required to operate the industries and cost of marketing the service. This enables the local production near or even at the point of use. If the delivery of the final products exceeds the cost of transportation of raw materials, then cost advantages of producing might get reduced. New ventures are exploring niches and are continuously developing the AM ecosystem by facilitating the local AM manufacturing capacities that drops the barriers to access to market [54, 55].

Logistics management includes the flow of goods, services, information, and money from raw resources to the end user and holds a small part in the manufacturing industry while supply chain is a wider term that refers to the sourcing of raw materials, the procurement of consumer requirements, the processing of raw materials into finished products, and timely delivery to consumers [56, 57]. But both the teams are based on innovation and for this they need to be equipped with AM technology. Startups such as Shiprocket Cogoport StackBOX are expanding their horizons by implementing AM technology [58, 59]. Some manufacturing industries also pay penalty for not delivering before the stipulated time and this hampers the cost production thereby impacting the economy. However, these perspectives are remunerated with several limitations. According to economic theory, a firm should expand production until the point where marginal cost is equal to marginal revenue [60, 61]. At each manufacturing level, marginal cost includes all costs such as material costs and energy intensity that vary with the different levels of production. However, the marginal cost lessens owing to the availability of additional suppliers in the markets or firms and low production speed. AM is unable to exploit economies of scale when the product varieties can be increased without additional costs as it is unlikely to manufacture the standardized parts [62–65]. AM does not guarantee the product qualities more often and this also leads to dissatisfaction of buyers, thereby discontinuation of potential buyers. These factors indirectly possess severe risk to the AM technology. Another factor which plays a vital role is the issuing of property rights as AM is based on computerized digital product designing where a simple 3D data can be transformed into a physical product just like the document getting printed from a computer consequently affects the economy of AM technology and should be taken into consideration [3, 5]. As AM technology uses a blueprint as a non-material entity for printing, it is considered as the vital component in the overall AM technique. Hence, safeguarding the designs involve extensive and costly actions.

Considering the above, one can reasonably state that the AM is not a "one size fits all"—solution, when it comes to deciding the most suitable method of manufacturing on a technical process level.

2.2 AM's Key Principles for Manufacturing Firms

It is a fact that AM technology can convert any simple 3D data into a physical product, hence can be considered as a versatile manufacturing unit. This has huge contribution to manufacturing industries in all levels and mostly AM offers the flexibility to customize a product without the need of tools and mold reducing the sunk costs [66–68]. AM technology modifies the product sequence and volume without cost penalty during the manufacturing process and offers complex designs for less cost i.e., large scale of products can be manufactured without involvement of more work and costs [69]. Lastly, AM reduces the requirement of assembly works during the production of a step by step integrated functional design [70, 71]. As there are other technologies available with the manufacturing industries and all of them have advantages and disadvantages, it is always important to prefer the technology on basis of strategy of production. From the economic perspective, till date only a few manufacturing industries have implemented AM technology and to examine the economic impacts certain models are recognized and proven [72]. It can be noted that contrary to conventional manufacturing, the economies of scale in AM technology are most often limited, as the cost of raw materials typically have a direct relationship with the production volume [73, 74].

One such model which can illustrate the economic impact of AM technology on manufacturing industry is Disruptive Business Model Development. Whenever a manufacturing industry is set up the idea behind it is to apply some technologies to gain the highest business value potential and these are more likely to be comprised in printing the assembled or the complete part of the whole product [75–77]. This is where the economy lags owing to the rapid manufacturing of the applications. Hence, if a manufacturing industry must implement AM technology, it has to be universally accepted and applied in all fields of that industry so that a large portion of manufacturing has to be focused on the AM technology itself. Analyzing any model will help markets to improve their responsiveness and quality through advanced technologies in the manufacturing process but to have a successful firm will only be possible if the market industry has a proper and strong business strategy [67]. To counter the continuous changing business environment, manufacturing industries must take decisions to keep all the values and functions organized and updated. complementary effects of AM technology with manufacturing, marketing, design, and organization make it highly profitable.

2.3 *AM's Impact on Manufacturing Technology in Job Creation*

The next thing to examine is the impact of AM technology on a manufacturing industry in job creation. This allows us to investigate the rising demand for western made manufacturing and the major factors that contribute to the economic aspect for job creation are (i) advent of AM technology in western economies, (ii) rising wage-levels in emerging economies, (iii) falling quality of business milieu in emerging economies, and (iv) rising demand for western-made manufacturing [17, 78–80].

The cost of producing much smaller batches of a wider variety, with each product tailored precisely to each customer's whims is falling. Manufacturing industries are now entering a new phase of customization-oriented production that is less concerned on traditional mass-production. This paves a way for cost advantages on economies of scale via efficient production due to cheap suppliers. This has also led to increasing manufacturing in western countries and growth of manufacturing industries. AM technology has shown its impact both in prototyping (faster and less waste) and also in production phase (especially in low volume and extremely complex products) [81, 82]. In addition, AM technology has always been profitable when it comes to the production cost and cost penalty. Also, incorporating this technology along with faster delivery will be beneficial for local suppliers over the foreign competitors [4, 5]. AM technology is also capable of generating lesser waste as compared to other conventional methods and this plays a key role in production process and growth. Another factor which contributes to the expense is the transportation cost [3]. Research shows that a lot of problems arise due to the transportation cost and emergence of technologies such as AM technology which involves a comparatively less labor as well as transportation costs. This results in profitable productivity. Employing people to meet the requirement due to AM technology towards customized products in large scale adds to the economy [10, 83, 84]. Hence, AM creates more opportunities for employment of people with different skills by boosting service provider jobs in manufacturing industries as AM needs highly skilled labor owing to its advanced machinery. The thrust areas where AM technology needs to be considered are the pre-production and post-production stage. The former one deals with the designing of a product and its manufacturing implementing the AM technology and the later one deals with the quality control and to what extent the repeatability of a fabricated part can be carried out. Manufacturing industries contribute to the job creation in several fields and implementation AM has created a lot of business opportunities [85, 86].

2.4 AM's Key Principles Applied to the Payoff Function

A payoff function usually is a visual representation of all the possible outcomes that can occurs when two people or groups must make a strategic decision and this decision affects the outcome of opponent's choice [87]. The payoff function was presented by Milgrom and Roberts in 1990 and deals with the production flexibility on manufacturing industries. Milgrom and Roberts assumptions on reducing the order receipt, lessening the production time, faster delivery, marginal cost production and extra setup costs for new designs might not lead to increased capital costs which was contrary to AM technology as it disconnects with various decision variables from primary cost constraints [88, 89]. Engaging AM in manufacturing industries allow the flow of digital information along the value chain from product design to production thereby reducing the time and setup costs. However, if a manufacturing industry prefers to implement better and advanced AM technology then it will involve a higher capital [90].

Alternatively, the economy that is envisioned consists of one industry. Forgetting the entry threat by a manufacturing industry by using additive manufacturing for the moment, at first the impact of AM is a monopoly with an incumbent that can offer customized and differentiated products [78]. But according to the aforementioned model, AM will never produce monopolistic markets, and this helps to focus on the effects of AM on market structure considering the industry level perspective.

2.5 *AM's Impact on Market Structure Models*

The new advancements in the technologies have affected the economy of the manufacturing industries by increasing the flexibility and this has been profitable strategically [91]. Flexibility generally includes product, volume, new product design, and faster delivery whereas product flexibility indicates the capability of manufacturing industry to efficiently shift capacity from the production of one product to another. Flexibility in terms of volume refers to a firm's ability to effortlessly change production output at minimum cost penalties. New designs in product flexibility facilitates rapid and efficient change of machinery setups when we modify the product specifications [92–95]. Studies indicate that the flexibility of manufacturing industries has varied its dimensions and has balanced it completely. As mentioned earlier AM being a versatile manufacturer allows the direct manufacturing of digital 3D models [92]. In addition, it offers flexibility in manufacturing by fulfilling the demands of products to meet the individual's customized needs. From the economic aspect, flexibility in modifications, product design and manufacturing lessens the modification costs [92–94]. This enables the manufacturing industries to understand and recognize the scope for economy in differentiating the product. While developing a new product, usage of AM technology not only reduces the sunk cost but also lessens the iteration cost during the development of new product [95].

Generating a firm involving AM technology requires a marginal production cost which is greater than the other flexible manufacturing technologies. So when this firm is created it includes onetime sunk cost to manage the resources and development whilst the production costs for the AM firm are chosen in such a way that the firm can serve certain market segments. Therefore, in case of AM the marginal production costs are lower than the costs of modifying a base product. So, the firm is now able to sell the product in these segments at a price between its own marginal cost of production and the second-smallest marginal cost of producing that product. Now when generating or involving of AM technology happens in a manufacturing industry, profits exceed the sunk cost and there is decrease in market prices. This is due to the marginal cost of production in AM technology and reduced price between the mergers and incumbents. Industries or firms which do not involve AM technology can increase market shares by producing extra products and decreasing the price of base products. This solely reduces the profit and reduced market prices. Motivations to include AM technology can lead to advancement in technology, low marginal costs, and reduced market prices [96]. When the marginal cost is low, other costs like supply a delivery cost will be predominant. Also, another cost factor which adds to the feature of AM technology is the cost of re-anchoring products. As AM involves flexibility in customization of products without cost penalty, so infinite variety of products and designs can be processed by the manufacturing industries which will reduce the re-anchoring costs [97, 98].

3 Conclusion

Hence, we can conclude that AM technology will lead to higher marginal cost of production as compared to other conventional technologies. Even if manufacturing industries implement the AM technology, there will be certainly some space for the emerging firms that produce niche products using other manufacturing technologies. The manufacturing industries should however assess the market structure by incorporating AM technology and consider strategies and processes to build profit from the continuously changing markets.

George Stigler known for the leading authority in price theory has suggested that flexibility is not a free good but also does not require that economies [99]. As mentioned earlier allowing flexibility by implementing AM in manufacturing industries is inadequate, and since markets are inevitably structural, it can never be structure-free when based on role playing. Economy is one of the human society's most basic arrangement of institutions whereby human beings in a society interact and live and solution to scarcity or any kind of shortage is solely based on economic policies and require proper strategies. Flexibility in social structures does not let economy to evade. This will deliver an effective natural order and there is no point to enhance the flexibility in manufacturing process if the demands are certain and sufficient similar products are created. However, it depends on how advanced manufacturing technologies are engaged in the firms or industries as the growth or decline in the manufacturing industries are dependent on better product variety, demands of costumer for desired products and uncertainty. Hence it is necessary to distinguish the applications which are expected or proven to be profitable for AM technology considering the perspectives of producers and costumers. To make profit by implementing AM, manufacturing industries should reduce the development costs, lessen delivery time, and shorten the capital intensity. Manufacturing industries should also focus on rapid manufacturing. In more detail, AM technology is the recent revolution in the manufacturing industries and using the manufacturing skills with novel technologies add to the economic competitiveness. Its fundamental concepts are associated with five key principles that depict the opportunities in manufacturing, and expanding the key characteristics of implementing AM. Firstly, AM is a versatile Technology that transforms any digital 3D model to a physical product layer by layer without the use of tools and molds. Secondly, the flexibility in manufacturing and customization according to the requirements of the costumers do not bear cost penalty. Next the complexity in manufacturing the product is free, reusing the customizable production is possible and this doesn't involve any additional costs. Lastly, the fifth key point that adds to the aspect of economy in manufacturing industries is the production of functionally integrated products. We have further analyzed that manufacturing industries with AM have higher flexibility and greater potential of manufacturing more variety of products. Owing to the capital investment for manufacturing a product market barrier also perform a major part. This leads to overall contestable markets.

Product attribute models sets out for strong scope of economy in differentiation of products involving AM technology. This is indicative of the fact that AM is efficient of producing fully functional parts in a wide range of materials including metallic, ceramic, polymers and their combinations in the form of composites, hybrid, or functionally graded materials as soon as it enters the market. This provides the costumers the product on basis of their choice or to choose amongst varied products. However, provided the low probability of mergers or cartel, prices are lowered accordingly. Game theoretical approaches usually are based on the combination of blockchain with other technologies and this shows that AM is capable to serve numerous market segments and hence, hindrance due to mobility reduces owing to the technological advancement of AM in manufacturing industries. These industries are also capable of serving preferences of costumers and deliver the products in stipulated time. Contemplating this manufacturing industries should adopt AM to increase their flexibility to get potential economic effects. Besides, the benefits of AM, there are several cost factors associated with AM technology. To setup the technology requires capital and this increases with installation of advancement in technology. Also, different element contributes to the firm's payoff function. If a firm is based on per unit production cost, then economy will be less as compared to large scale production. To meet the varying costumer's requirement, adjustments and strategies must be planned to get maximum benefits. Some technical constraints also prevent manufacturing industries to engage AM technology, and this will restrict the industries to make profits. And also, industries need to make decisions to invest more capital to meet the required varying taste of the costumers.

Taking all these key points we can suggest that manufacturing industries should efficiently leverage AM as a new source of modern manufacturing. Apart from the existing production management system, AM effects certain adjoining fields such as innovation management, marketing, business policy and strategy. Challenges for multidisciplinary research, will have strong potential effect on the impact of AM technology on producers and markets. Therefore, one should quantify AM technology implications on production-related costs including upward and downward transactions in the supply chain. The ability of costumers to produce themselves is another demand in the field of AM technology as they have access to digital designs of the customized products and AM technology allows to transform the designs to reality. This disrupts the market structure and affects the economy. Therefore, both manufacturing industries as well as consumers should do sufficient research before implementing AM technology.

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Chapter 16
General Job Opportunities for the Graduates, Post Graduates and PhD Graduates in Additive Manufacturing Industries

Rajashree Samantray, Manisha Priyadarshinee, and Shashanka Rajendrachari

Abstract Additive manufacturing (AM) or 3D printing process are varied from traditional manufacturing technique. The past decade has utilised this futuristic technique in a wide range of applications in industries. Starting from rapid prototyping in initial times to advanced end use customised products, 3D printing has grown really fast. It is believed by the researchers that AM is going to be as popular and revolutionary as cyberspace and healthcare. Added substance fabricating gives everyone such opportunities from a digital plan for making actual 3D items. While an innovation headway perspective is imperative for guaranteeing thriving, improvement in the monetary viewpoint offers the need for development. AM has shown its development in the two perspectives because of extraordinary expansion in private and modern applications. However, the uses of added substance fabricating innovation are still in an essential stage in non-industrial nations. This undertaking has presented the various chances of AM innovation for the non-industrial nations and conceivable outcomes utilization. A study was headed to identify the plans and prospects for the present generation and the upcoming one.

Keywords Additive manufacturing · Industries · Job opportunities · Graduates · AM professional

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1 Introduction

A creation of a three-dimensional body with layer-by-layer form, through computer-aided design (CAD) is called as rapid prototyping technique. The technology was well adopted and functionalized in 1980, helped technologists understand a 3D image before creating actual product. This is otherwise known as Additive manufacturing process (AM). The benefits that AM gave to the human being are, saving cost and time, better presentation of human thoughts and creativity and advancement of product and manufacturing. In the present era, with fast availability of better technologies day-by-day, the 3D printing has started to diminish in the manufacturing industry. However, the system is now widely used by the scholars, instructors, scientists, artists, clinicians, market investigators and so on [34]. The AM process helps students and researchers for preparing models and analysing them for a purpose of better knowledge theoretically and comprehensively. Doctors are using 3D printing to analyse patient's body to understand issues and finding out ways to solve them. The market analysers investigate about a new product and understand its review in market, which helps them understand the need of the customer and do modifications prior manufacturing the final product. In 3D printing, a prototype is prepared digitally with CAD software. There is no need to remove any materials, creating a model with layer over layers to get a final picture of the object. The AM helps making objects with complex structures and designs effortlessly at a short time in an inexpensive way.

2 Applications of Additive Manufacturing

The endless opportunities come across, when three major segments such as knowledge, imagination, expertise meet. AM is broadly used in dentistry, manufacturing, biomedical sectors, designing, architecture and so on. Among the several uses of AM, a few mentions by researchers are discussed here. In the field of construction, AM have been used in processes like contour constructing, concrete printing, polymers preparation, which all resulted efficient application, cost effective and time consuming [33]. Past few years have experienced a major breakthrough in manufacturing sector due to AM. With huge contribution in the field of science, research and technology, 3D printing technology have helped personally and industrially. As far as the benefits are concerned, it is broadly used in many countries. Yet, some under-developed or developing countries are not that benefited. The countries need to understand and explore AM to get its advantages. In order to explore the requirement of AM, there is a prerequisite of wide opportunities in the field. A study is presented here discussing the future scope of 3D printing or additive manufacturing.

3 Career Options in Additive Manufacturing

The AM demand is increased so high that the need of professionals in the domain is further amplified. The advancement of the subject has involved industries ranging aerospace to automotive sectors. There is no such specific career guideline for AM, while it is well adapted to people who learn using it. The newness of the technology has opened plenty of openings for people having grasp in it. The AM professionals need not have any particular career path, they can have any route in their career and opt for it. However, with the changed scenario and growing demand of AM, there is a specific type of career and several resources present, to prepare one to be a professional and get a job in huge options of job market.

4 Skills Needed to Be an AM Professional

Among the several expertise needed to be a professional, few highlighted skills are the most desired and asked in job sector. Starting from technical hold to grasp in soft skills, AM covers many more areas, because of its broad reachability in every sector. Few needs are included here [18]:

- A good knowledge in math, problem solving, trigonometric skills.
- Strong software skills, like design software, optimization techniques and so on.
- Few mostly used software like computer aided design (CAD), CNC Milling, design for additive manufacturing (DFAM) etc.
- Familiarity in material science, sound knowledge in metals and non-metals, along with common manufacturing skills like welding joints, casting, milling, drilling, turning and so on.
- Some of the supporting techniques for 3D printing such as lasers, 3D modelling etc.
- In addition to problem solving, troubleshooting skills, good communication, team player, prioritizing work, work life balance are few important skills one should have.
- One should possess curiosity and passionate to learn things, a positive willpower is a strong additive in job market.

5 Degrees and Certificates for Additive Manufacturing

Since there are no particular degrees are offered to be familiar in AM, yet there are some AM related programs that specify AM learnings through training programs. Some of the US based courses are, Additive manufacturing program by Westmoreland county community college [4], Master of science (MS) in additive manufacturing by college of engineering mechanical and aerospace engineering, Miami [26], Master of Engineering in AM by University of Cincinnati [23], Professional and distance education in AM provided by the Ohio state university [3], M.E. program on additive manufacturing and design by Penn State world campus [5] and so on.

There are various range of certificate programs, planned and prepared to improve skills of people, making them ready to implement AM to face the great demand of the subject. The programs include world class trainings to make the students ready for better problem solving with advanced technical skills. Basically, with overall AM and an understanding of industry-based AM are comprised in the entire course. To name a few programs [18], AM certificate program by ASTM centre of excellence, AM official certificate program provided by Central Connecticut state university, AM technician: 3D printing to industry, AM by Colorado school of mines, 3D digital design and AM technology, Purdue AM certificate and so on.

6 Jobs and Opportunities

With the increased AM demand, a wide range of additive manufacturing start-ups and businesses have grown in the last decade. In addition, some huge sectors have opened their AM wing due to popular market demand. The opportunities keep popping on job provider platforms LinkedIn, indeed etc. Apart from the above-mentioned media, there are a plethora of platforms that gets a candidate to apply through the websites directly. To name a few, ASME career centre [10], SME featured jobs in manufacturing [28], Women in 3D printing [31], WIM virtual career fair [32] etc.

On talking about what titles an AM professional can acquire in any field, the answer would be many. The topic of 3D printing can give a candidate many more options. Among the various listings, the image below provides plenty of job listings for an AM professional (see Fig. 1).

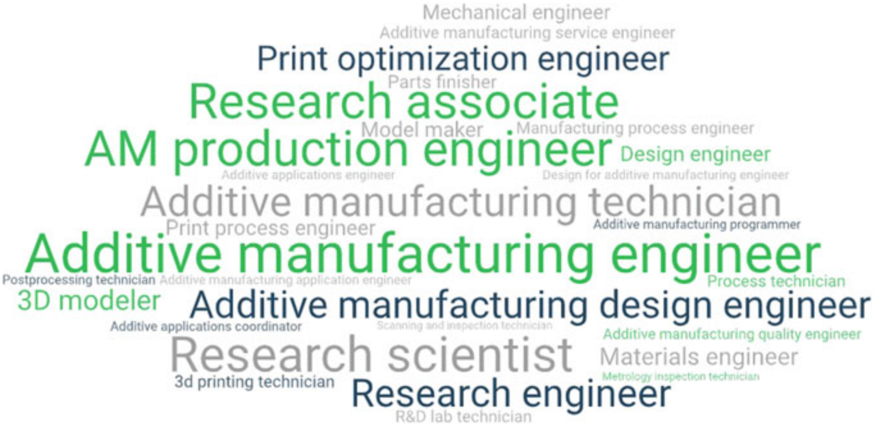

Fig. 1 List of job offers an AM can have [22]

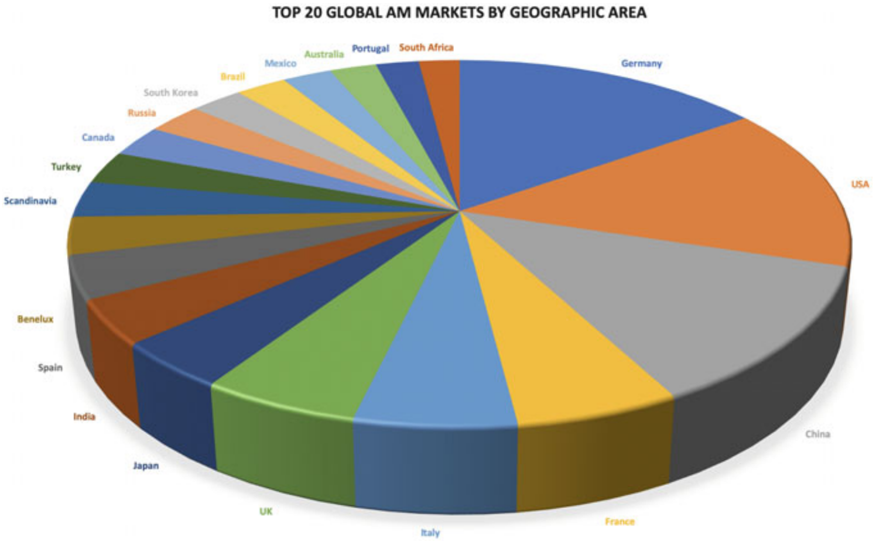

Fig. 2 Additive manufacturing global market, top 20 countries to have huge contribution in AM (data in millions of US dollars) [2]

Additive manufacturing technology or 3D printing make huge profit for its reasonable and profitable features. As per research and forecast, AM global market, which was $1.9 billion at 2016, is forecasted at $20.9 billion for 2024. Improvised design, better technology implementation, optimum use of structural metal parts implies market growth [17]. Top countries that generate 65% of the revenues in the field of AM or 3D printing are, Germany, USA, China, France, Italy, UK, Japan, India, Spain and Benelux countries [2]. A figure presenting top 20 countries in the world, that contribute in a massive amount in AM, is provided in Fig. 2.

7 Additive Manufacturing Companies Across the World

The additive manufacturing technology is exponentially growing day by day in a multiple direction including health sector, locomotive, aerospace and so on. The technology is not limited to designing or prototyping anymore. It has further moved beyond that, considering the fast-growth of the manufacturing chain and demand. Some of the frontline companies in the AM field, recognized world-wide are as follows,

1. Stratasys Ltd. [20]
2. Materialise NV [25]
3. Autodesk [12]
4. HP [14]

5. Markforged [19]
6. Fast Radius [16]
7. Conformis [21]
8. GE Additive [6]
9. 3D Systems [1]
10. Canon [13]
11. Carbon [29]
12. Desktop Metal [15]
13. Made in space [24].

8 Additive Manufacturing Companies in India

The list of top emerging AM companies in India are provided below [30]. Among the printing services, the companies manufacture and distribute 3D printers, organize training programs and so on.

1. SolidCAM INDIA, Pune, Maharashtra
2. JGroup Robotics
3. Stratasys India
4. Think3D
5. Imaginarium
6. Novabeans
7. Altem
8. Brahma3
9. Divide by zero technologies.

With the diversified growth in additive manufacturing in industries, the educational institutes are now coping up to meet the level. Some of the opportunities are implemented for students to make them aligned with market prospects. The AM technology has now emerged up to a certain level where it is being used in health sectors as prosthetic advances, as well as in infrastructures and designs. In order to match with the market scenario, the technology is getting advanced day by day, with a target of mass production. Some of the educational institutes are implementing AM degrees to replicate the market demands. In addition, the academia is moving forward to collaboration with industries, to educate the students about the real time problems, implementations and applications in 3D printing technologies. The hands-on technology skill makes the graduates to understand and practice the technology with better experience.

9 Professional Bodies on Additive Manufacturing

There are associations or professional bodies, that aim to promote the AM technology or 3D printing further in India and all over the world. These communities support and encourage continual growth of the domain in industry as well as education aspect. Among a plethora of the active programs, to name a few, organizing seminars and conferences, educational curricula, initiating new market strategies and developing research in AM. They provide certain rules for people to join their community. One with certain level of experience in AM, involved with research in the segment can join the societies. The AM companies, market suppliers, industry professionals, researchers are encouraged to join such bodies. Some of the major societies include,

1. Additive Manufacturing Society of India (AMSI) [7]
2. Additive Manufacturer Green Trade Association (AMGTA) [8]
3. Association for Additive Manufacturing Technology (AMT) [11]
4. Additive Manufacturing-UK (AMUK) [9]
5. SME AM Technical Community [27].

The above-mentioned societies or communities help and support the additive manufacturing or 3D printing technology across the globe. The coming decade will experience a hike in the usage and applications in AM. With increasing demand, the academia will implement the AM-friendly programs or courses more and there will be much more industry collaborations, more job openings and increased technology awareness.

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